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Division of Chemical Science

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BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

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SYNTHESIS AND STUDY OF THE PROPERTIES OF LITHIUM PEROXIDE DIPERHYDRATE

S. Z. Makarov and T. A. Dobrynina

Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
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A study of solubility in the system $LiOH-H_2O_2-H_2O$ over the temperature range from − 21 to + 30° in the region of high hydrogen peroxide concentrations in the liquid phase revealed the existence of a previously unknown compound, namely, lithium peroxide diperhydrate $Li_2O_2 \cdot 2H_2O_2$ [1]. It was not possible to obtain this compound by the direct action of concentrated hydrogen peroxide on lithium hydroxide. The reaction of 75% H_2O_2 with $LiOH \cdot H_2O$ at 0 and −18° resulted in the formation of lithium peroxide hydrate monohydrate $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$, while the action of 85% H_2O_2 on $LiOH \cdot H_2O$ was normally accompanied by violent decomposition of the reaction mixture at 0° and the formation of only $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ at −18°.

EXPERIMENTAL

For the preparation of $Li_2O_2 \cdot 2H_2O_2$, $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ was treated with concentrated hydrogen peroxide at low temperature. The precipitates obtained were filtered from the mother liquor with cooling in an ice-salt

TABLE

Data from Experiments on the Synthesis of Lithium Peroxide Diperhydrate $Li_2O_2 \cdot 2H_2O_2$

Expt. No.	Initial H_2O_2 concentration in weight %	Experiment temperature, °C	Composition of preparations obtained, %					$Li_2O_2:H_2O_2:H_2O$ in moles	Comments
			act.O_2	Li	Li_2O_2	H_2O_2	H_2O		
3	88,20	0	31,00	7,68	25,38	47,09	27,53	1:2,51:2,76	Decomposed after 5 days at -2°
1	88,20	—15	34,83	11,36	37,54	49,90	12,56	1:1,79:0,85	Decomposed immediately after preparation
2	88,20	—20	35,04	6,78	22,40	57,89	19,71	1:3,49:2,24	Decomposed after 2 days when stored at 0 to -20°
4	95,00	—21	37,60	5,60	18,50	66,22	15,28	1:4,83:2,10	
5	95,00	—21	38,49	5,72	18,90	67,82	13,28	1:4,85:0,79	
6	94,50	—15	37,05	5,41	17,87	65,52	16,61	1:4,95:0,24	Preparation stored without decomposition over liquid nitrogen

mixture and washed with a small amount of cold ether. Table 1 gives data from experiments on the synthesis of $Li_2O_2 \cdot 2H_2O_2$. As chemical analysis showed, the preparations obtained contained a large amount of mother liquor which could not be washed out with cold ether as the $Li_2O_2 \cdot 2H_2O_2$ preparations decomposed during long washing. $Li_2O_2 \cdot 2H_2O_2$ preparations containing mother liquor were extremely unstable at room temperature and remained unchanged under these conditions for not more than 15-20 minutes. The vigorous decomposition with strong heat evolution and frothing resulted in the formation of a solution of lithium hydroxide. When stored at − 2°, $Li_2O_2 \cdot 2H_2O_2$ preparations containing mother liquor decomposed to lithium peroxide hydrate monohydrate over a period of a few days. The composition of preparation No. 3 after storage for five days at − 2° was as follows:

Act. O_2, %	Li, %	Li_2O_2, %	H_2O_2, %	H_2O, %	$Li_2O_2 : H_2O_2 : H_2O$
22,90	8,42	27,82	28,06	44,12	1 : 1,01 : 2,99

Storage of $Li_2O_2 \cdot 2H_2O_2$ preparations containing mother liquor in a closed tube in a Dewar vessel over evaporating liquid nitrogen did not result in decomposition.

To obtain pure $Li_2O_2 \cdot 2H_2O_2$ preparations free from mother liquor, we investigated their vacuum drying at room temperature (18-21°) and at 0 to − 2°. A $Li_2O_2 \cdot 2H_2O_2$ preparation containing mother liquor was placed in a bottle in a vacuum desiccator over phosphorus pentoxide and kept at the required temperature. The residual pressure in the vacuum desiccator was approximately 10 mm Hg. After definite time intervals, the preparation was analyzed for active oxygen and lithium.

TABLE 2

Data on the Removal of Mother Liquor from $Li_2O_2 \cdot 2H_2O_2$ in Vacuum at 0 to − 2°

Vacuum drying time, days	Composition of preparations obtained					$Li_2O_2 : H_2O_2 : H_2O$ (in moles)
	act. O_2	Li	Li_2O_2	H_2O_2	H_2O	
Initial	41,30	9,22	30,46	65,23	4,31	1 : 2,89 : 0,36
3	41,17	9,44	31,18	64,42	4,40	1 : 2,79 : 0,36
4	41,85	9,54	31,52	65,61	2,87	1 : 2,81 : 0,23
7	41,50	9,91	32,75	63,95	3,30	1 : 2,64 : 0,26
10	41,56	10,30	34,04	63,12	2,84	1 : 2,50 : 0,21
15	40,99	11,78	38,92	58,29	2,79	1 : 2,02 : 0,18

TABLE 3

Data on the Removal of Mother Liquor from $Li_2O_2 \cdot 2H_2O_2$ in Vacuum at 21°

Vacuum drying time, days	Composition of preparations obtained					$Li_2O_2 : H_2O_2 : H_2O$ (in moles)
	act. O_2	Li	Li_2O_2	H_2O_2	H_2O	
Initial	41,30	9,22	30,46	65,23	4,31	1 : 2,89 : 0,30
1	41,30	9,78	32,32	63,84	3,84	1 : 2,66 : 0,30
3	38,90	15,54	51,34	44,65	4,01	1 : 1,20 : 0,20
4	36,47	16,18	53,46	37,91	8,63	1 : 0,95 : 0,41
7	37,74	15,94	52,66	41,20	6,14	1 : 1,06 : 0,30

The active oxygen was determined with permanganate and the lithium was determined acidimetrically by the procedure we described previously [1].

Data on vacuum drying of $Li_2O_2 \cdot 2H_2O_2$ preparations containing mother liquor at 0 to − 2° and 19 to 21° are given in Tables 2 and 3 and graphically for 0 to − 2° in Fig. 1, where the vacuum-drying time of the preparation in days is plotted along the abscissa axis and the number of moles of H_2O_2 (curve 1) and H_2O (curve 2) per mole of Li_2O_2 (n) is plotted along the ordinate. As the data on vacuum drying of $Li_2O_2 \cdot 2H_2O_2$ show, the removal of mother liquor from the preparation at 0 to − 2° proceeded gradually and hardly affected the hydrogen peroxide of the compound. After 15 days, we obtained a $Li_2O_2 \cdot 2H_2O_2$ preparation whose composition was close to theoretical ($Li_2O_2 \cdot 2.02\ H_2O_2 \cdot 0.18\ H_2O$), while the removal of mother liquor from $Li_2O_2 \cdot 2H_2O_2$ preparation in vacuum at 19 to 21° (Table 3) involved decomposition of the compound $Li_2O_2 \cdot 2H_2O_2$ to the partly hydrated compound $Li_2O_2 \cdot H_2O_2$.

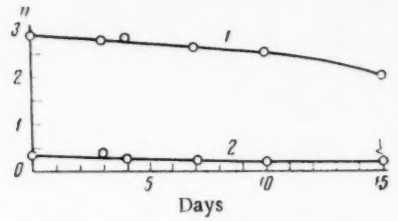

Fig. 1. Curves of the removal of mother liquor from $Li_2O_2 \cdot 2H_2O_2$ in vacuum at 0 to − 2°. 1) H_2O_2; 2) H_2O (n is the number of moles of H_2O_2 and H_2O per mole of Li_2O_2).

TABLE 4

Data on Interplanar Distances for $Li_2O_2 \cdot 2H_2O_2$

Intensity, I	d, in A
V. w.	3.54
Av.	2.93
Av.	2.61
Av.	2.23
W.	1.47

The chemical individuality of lithium peroxide diperhydrate $Li_2O_2 \cdot 2H_2O_2$ was confirmed by investigation of this compound by differential thermal, and qualitative x-ray phase analysis.

A thermal investigation of the decomposition of $Li_2O_2 \cdot 2H_2O_2$ [2] showed that this compound is unstable and when heated to 50-60° for 15 minutes, it decomposes vigorously losing hydrogen peroxide of crystallization; it changes into anhydrous lithium peroxide at 85-100°.

The x-ray diffraction investigation * of the compound $Li_2O_2 \cdot 2H_2O_2$ was carried out by Debye's method in a special camera cooled to − 45° with liquid nitrogen vapor. Table 4 gives data on interplanar distances found for the compound $Li_2O_2 \cdot 2H_2O_2$.

The data obtained indicate the presence of an independent structure which differs from the structure of other peroxide compounds of lithium [3-7].

SUMMARY

1. Lithium peroxide diperhydrate $Li_2O_2 \cdot 2H_2O_2$ may be obtained by the action of concentrated hydrogen peroxide on lithium peroxide hydrate monoperhydrate $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ at low temperatures.

2. $Li_2O_2 \cdot 2H_2O_2$ preparations are stable only when they are completely free from mother liquor. The mother liquor may be removed from $Li_2O_2 \cdot 2H_2O_2$ preparations in vacuum at low temperatures.

3. The individuality of the compound $Li_2O_2 \cdot 2H_2O_2$ was confirmed by differential thermal and qualitative x-ray phase analyses.

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* The qualitative x-ray phase analysis of $Li_2O_2 \cdot 2H_2O_2$ was carried out by G. A. Gol'der.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

NEW DATA ON THE EFFECT OF RADIOACTIVE RADIATION ON SOLIDS AND EXTERNAL RADIATION ON SOME HETEROGENEOUS CHEMICAL PROCESSES

Vikt. I. Spitsyn

Institute of Physical Chemistry, Academy of Sciences of the USSR
Report to the General Conference of the Division of Chemical Sciences,
Academy of Sciences, USSR, Moscow, April 20, 1960
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In 1958, the author and his co-workers gave the first information on the effect of radioactive radiation of solids on some heterogeneous processes, namely, isotopic exchange and adsorption from aqueous solutions [1-3]. At the same time, it was established that the introduction of radioactive sulfur into a catalyst for the dehydration of cyclohexanol (a mixture of $MgSO_4$ and Na_2SO_4) considerably increased its catalytic activity [4]. Continuation of these investigations completely confirmed the initial observations. Radiochemical activation of the surface of solids occurs at much lower radiation dose strengths than are required for true radiation chemical processes (decomposition, oxidation-reduction, etc.). The emission of α- or β-particles by solids apparently leads to continuous formation on their surface of many crystal-lattice defects and also ionized and excited atoms, which play the part of charged active centers.

New data were obtained on the effect of radioactive radiation of S^{35} on the rate of isotopic exchange in some heterogeneous systems. The isotopic exchange of sulfur in the system of $K_2\overset{*}{S}O_4-SO_3$ at 840° was investigated over a range of specific radioactivities of potassium sulfate from 0.02 to 131 mC/g [5]. The apparatus and experimental procedure were analogous to those described in [2]. The results obtained are given in Fig. 1. The isotopic exchange of sulfur in the system studied was divided sharply into three phases. A study of the system $Na_2\overset{*}{S}O_4-SO_3$ led to analogous results. In this case, we measured the rate constants of exchange over the temperature range 700-840°, which made it possible to calculate the activation energy of the process. For preparations with a specific activity of 0.02-1 mC/g, it was found to equal 23-24 kcal/mole and for preparations with an activity of 10-25 mC/g, it equalled 18-19 kcal/mole.

In the given systems, isotopic exchange apparently proceeds through the reaction of SO_3 with SO_4^{2-} ions on the surface of sulfate and the formation of $S_2O_7^{2-}$ ions as an unstable intermediate compound. The conditions for their formation will be more favorable with an increase in the number of positive charges on the surface of the solid phase, caused by the continuous emission of β-particles. It may be considered that this is the reason for the increase in the rate of isotopic exchange over the range of specific activities of potassium sulfate from 0.05 to 2 mC/g. The fall in the degree of isotopic exchange for preparations with a specific activity of 3-35 mC/g may result from rapid neutralization of the positive charges of the active centers by the copiously emitted electrons. In any case, the change in activation energy indicates a difference in these two stages of isotopic exchange.

The sharp increase in the degree of exchange with an increase in the specific activity of $K_2\overset{*}{S}O_4$ above 35 mC/g is probably caused by a mechanism differing from that for the first branch of the curve in Fig. 1. There are grounds for stating that in this case radiation phenomena caused by the β-particles emitted, namely,

ionization of SO_3 molecules in the gas phase and also increased activation of SO_4^{2-} ions and separate atoms of the sulfate crystal lattice, begin to play a decisive role. To check this hypothesis, we studied isotopic exchange in the system $K_2\overset{*}{S}O_4 - SO_3$ with potassium sulfate of low specific radioactivity but with external irradiation of the labeled preparation and SO_3 vapor with a beam of high-energy electrons from a betatron, whose design made it possible to obtain an external beam of electrons [6].

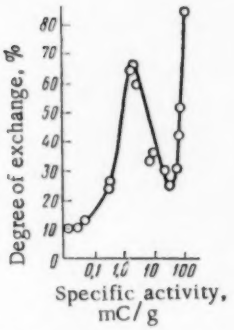

Fig. 1. Relation of the rate of isotopic exchange of sulfur in the system $K_2\overset{*}{S}O_4 - SO_3$ to the specific activity of $K_2\overset{*}{S}O_4$.

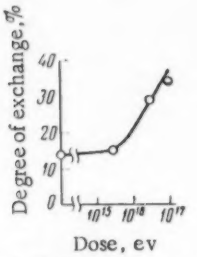

Fig. 2. Relation of the degree of exchange of sulfur in the system $K_2\overset{*}{S}O_4 - SO_3$ to the integral dose of external electron radiation of the K_2SO_4 preparation (after 10 minutes).

The investigation showed that external electron irradiation of the potassium sulfate and the gas phase in contact with it, containing SO_3, had hardly any effect on the exchange rate at a dose of the order of 10^{15} ev/10 minutes. An analogous dose is given by the β-radiation of a $K_2\overset{*}{S}O_4$ sample with a specific activity of the order of 2 mC/g, which, as was pointed out above, has a strong effect on the isotopic exchange rate. An increase in the dose of external radiation to 10^{16}-10^{17} ev/10 minutes led to an increase in the degree of exchange, which was directly proportional to the logarithm of the dose (Fig. 2). No signs of decomposition of the potassium sulfate were observed in these experiments. External radiation doses, at which the rise on the curve in Fig. 3 began, corresponded approximately to β-radiation doses obtained with a $K_2\overset{*}{S}O_4$ preparation with a specific activity corresponding to the beginning of the third section of the curve in Fig. 1. Thus, there seems to be no doubt about the connection between these phenomena.

It has been reported previously [1] that the radioactive radiation of S^{35} also affects the isotopic exchange of oxygen in the system $Na_2\overset{*}{S}O_4 - O_2^{18}$. In 1960, Spitsyn and Finikov studied this process in more detail with $Na_2\overset{*}{S}O_4$ preparations whose specific radioactivity lay within the range of 0.08-25 mC/g. The gaseous oxygen was labeled with O^{18} (1.5 at. %). The exchange experiments were carried out by the dynamic method in the temperature range 620-790°. The degree of exchange was measured with a mass spectrometer. The experimental procedure was analogous to that described in [7]. Figure 3 shows the relation between the degree of exchange and specific radioactivity of the $Na_2\overset{*}{S}O_4$ preparations.

The picture observed is very similar to that described for the exchange of sulfur in the system $K_2\overset{*}{S}O_4 - SO_3$. At 760°, the degree of exchange of oxygen from the inactive Na_2SO_4 preparation was approximately 1%. Under the same conditions, a preparation with an activity of 0.08 mC/g underwent 7.8% exchange. Maximum exchange was reached with a specific radioactivity of $Na_2\overset{*}{S}O_4$ equal to 1.6 mC/g (55.8%). There was then a sharp fall in the exchange rate (8.2% at 1.9 mC/g) and a slow increase as a result of a further increase in the activity (15.4% at 10.3 mC/g and 24.3% at 25 mC/g). It may be considered that, in the reaction studied, exchange proceeds through oxygen adsorbed on the surface of the solid sulfate. The three branches on the curve in Fig. 3 probably arise for the reasons examined for isotopic exchange in the system $K_2\overset{*}{S}O_4 - SO_3$.

Important results were obtained by studying the sorption of some organic dyes from aqueous solutions on a radioactive solid phase [1, 3]. The change in dye concentration was determined spectrophotometrically. In all experiments, a careful check was made to make sure that there was no radiolysis of the dyes used under the action of the radioactive radiation. Barium sulfate containing various amounts of S^{35} and, in some cases, radium was used as the sorbent. The introduction of S^{35} into the $BaSO_4$ preparations over the range of specific activities from 0.01-10 mC/g led to a decrease in the sorption of methylene blue and an increase in the sorption of acid orange in comparison with an inactive sorbent. The addition of radium had the directly opposite effect. It may be assumed that the observed change in the sorption of dyes was associated with the appearance of a positive charge on the precipitate of radioactive barium sulfate containing S^{35}, due to the continuous emission of β-particles, and a negative charge on a precipitate of $Ba(Ra)SO_4$, caused by the emission of α-particles from the crystal surface. Thus, the colored cations of the basic dye (methylene blue) must actually be sorbed less in the presence of a β-emitter and more in the presence of an α-emitter. The behavior of an acid dye, in which the anion is colored, must be directly

opposite. Experiments with another basic dye, namely, brilliant green, showed that it behaves analogously to methylene blue with respect to a radioactive sorbent.

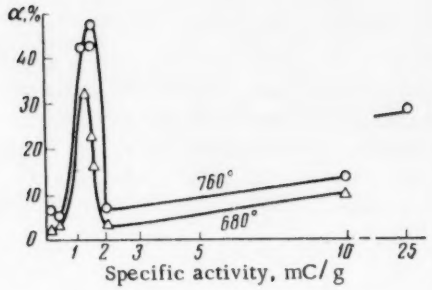

Fig. 3. Relation of the rate of isotopic exchange of oxygen in the system $Na_2\overset{*}{S}O_4 - O_2^{18}$ to the specific activity of $Na_2\overset{*}{S}O_4$.

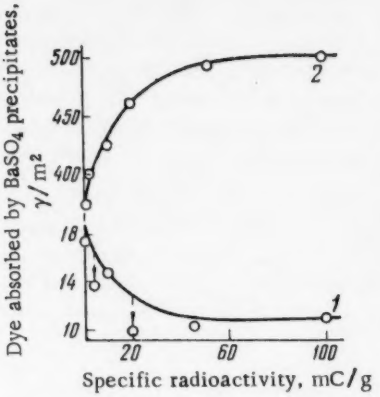

Fig. 4. Effect of the specific radioactivity of $Ba\overset{*}{S}O_4$ on the sorption of dyes: 1) methylene blue; 2) acid orange. The points marked with a broken line correspond to samples that had been kept.

In 1960, Spitsyn and Gromov extended the investigation to the sorption of dyes on $BaSO_4$ preparations with a specific activity of up to 101 mC/g. The results obtained were analogous to those obtained previously. The sorption of methylene blue decreased even more and that of Acid orange increased when highly active samples of barium sulfate were used. However, a new phenomenon was observed in this case: $Ba\overset{*}{S}O_4$ preparations of high activity, which had been stored for a long time (100-200 days) and had suffered a corresponding fall in activity, had a lower capacity for the sorption of methylene blue than freshly prepared samples of the same activity (Fig. 4).

Measurement of the specific surface of the sorbents studied by Deryagin's method showed that it did not change as a result of prolonged radioactive decay of S^{35} in the $BaSO_4$ preparations. Thus, it was necessary to conclude that, due to prolonged action of β-radiation, the storage of highly active samples of barium sulfate led to a decrease in the number of active adsorption centers on the surface of the sorbent without a change in the total surface.

This phenomenon was not detected so readily for Acid orange, as the sorption of this dye decreased with a decrease in the specific radioactivity.

In 1960 Spitsyn and Gromov also studied the effect of external radiation on the sorption power of barium sulfate. The initial $BaSO_4$ preparation was fired in vacuum at 300-350° in a special metal cylinder. It was then stored in a nitrogen atmosphere under a pressure of 5 atm to avoid the adsorption of atmospheric oxygen which could form ozone during irradiation. Irradiation with 800-kev electrons, obtained with a linear accelerator, was carried out in an aluminum cell with water cooling and flushing with nitrogen. The temperature was maintained within the range of 15-30°. In addition, we also studied irradiation with 1.5-Mev protons, obtained with a Van de Graaf electrostatic generator. These experiments were carried out in vacuum (10^{-5}-10^{-6} mm Hg). Despite cooling of the target with water, the preparation was still heated to 100-150°. No induced activity was detected in the samples after irradiation with protons.

The sorption powers of irradiated and unirradiated $BaSO_4$ preparations were studied at the same time. The investigation showed that with an increase in the absorbed integral dose of electron radiation, there was a considerable decrease in the sorption of both of the dyes studied, i.e., methylene blue and acid orange. It is interesting to note that by reducing the dose strength used and simultaneously increasing the treatment time it was possible to produce a considerable reduction in the sorption capacity of $BaSO_4$ at a lower integral radiation dose. Bombardment of barium sulfate with protons produced a much sharper fall in its sorption power than irradiation with electrons at the same dose strength. The decrease in adsorption of dyes by irradiated preparations of $BaSO_4$ was almost directly proportional to the dose of absorbed radiation (Fig. 5).

The $BaSO_4$ preparations which had been irradiated with electrons or protons did not undergo appreciable chemical decomposition. They acquired a light grey-brown color which disappeared after a week, but the sorption properties were not restored even after 20-25 days. The color disappeared after the sample had been fired for 1 hour at 200-250° and the sorption properties of the irradiated samples were almost completely restored. Measurement of the specific surface of the $BaSO_4$ preparations showed that it did not change as a result of irradiation. Thus, treatment of barium sulfate with high-energy particles, namely, electrons and protons, has a peculiar "polishing" action, which apparently leads to a decrease in the number of active centers which determine sorption properties on the surface of irradiated preparations. The facts presented should be borne in mind in attempts to prepare active solids by irradiation.

The first data have now been obtained on the effect of radioactive radiation of the sorbent on the adsorption of gaseous substances [8]. The experiments were carried out with powdered preparations of K_2SO_4, containing S^{35}. The adsorption of methanol vapor was measured with the apparatus described in [9]. The results are presented in Fig. 6. The adsorption of methanol by a $K_2\overset{*}{S}O_4$ sample with a specific activity of 17.2 mC/g was found to be 20% higher than with an inactive preparation. A $K_2\overset{*}{S}O_4$ sample with a specific activity of 0.08 mC/g in which β-decay had proceeded for approximately 500 days had a sorption power which was 40% higher than inactive K_2SO_4. Thus, not only the actual activity of the sorbent studied is important, but also the time that it has been undergoing radioactive decay. It should be mentioned that an analogous phenomenon, namely, an accumulation of the effect of radiation, was also observed for isotopic exchange in the system $K_2\overset{*}{S}O_4 - SO_3$ [1].

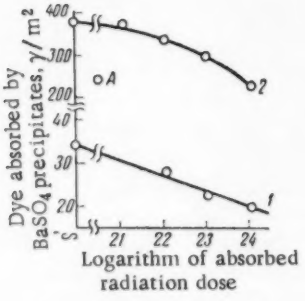

Fig. 5. Sorption of dyes by barium sulfate in relation to the dose of external electron radiation adsorbed by the precipitate: 1) methylene blue; 2) acid orange; point A corresponds to a $BaSO_4$ preparation irradiated with protons.

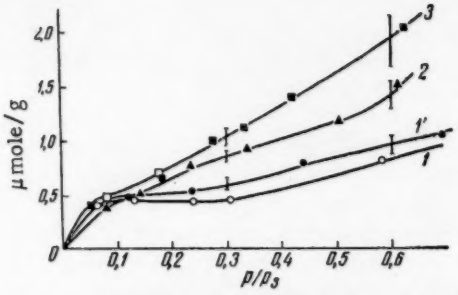

Fig. 6. Adsorption of methanol vapor on radioactive and inactive K_2SO_4 samples (25°): 1 and 1') inactive K_2SO_4 preparations; 2) radioactive $K_2\overset{*}{S}O_4$ preparation (17.2 mC/g) after storage for 30 days; 3) radioactive $K_2\overset{*}{S}O_4$ preparation (0.08 mC/g) after storage for 473 days. The black points refer to samples pumped out at 200° before the experiment and the others refer to samples pumped out at 20°.

We have made progress in our investigations on radioactive catalysts. It was established [10] that, during the decay of S^{35} forming part of a catalyst for the dehydration of cyclohexanol (a mixture of $MgSO_4$ and Na_2SO_4), the catalytic activity of the latter decreases in accordance with the law described in previous work [4]. This observation makes it possible to reject the hypothesis that chlorine formed by decay of S^{35} plays some part in increasing the catalytic activity of radioactive magnesium and sodium sulfates. On the other hand, it confirms the opinion put forward previously [4] that the actual β-radiation of the radioactive catalyst is the reason for its higher catalytic activity (Fig. 7).

Investigations showed that it is possible to introduce another radioactive isotope, which does not form part of the composition of the catalyst, into $MgSO_4$ instead of S^{35} and this increases the catalytic activity. Thus, for example, calcium chloride does not catalyze the dehydration of cyclohexanol. The addition of $CaCl_2$ to magnesium sulfate led to a strong decrease in the degree of conversion of cyclohexanol. However, the presence of the radioactive isotope Ca^{45} in $CaCl_2$ increased the catalytic activity of the mixture $MgSO_4 + CaCl_2$. The

effect of Ca^{45} at the same specific activity was greater than that of S^{35} and this was undoubtedly due to the fact that the maximum energy of the β-radiation of Ca^{45} (0.255 Mev) is greater than that of S^{35} (0.169 Mev). In any case, the activation energy of cyclohexanol dehydration was considerably reduced by the addition of radioactive $CaCl_2$ to magnesium sulfate. It should be added that experiments on the dehydration of cyclohexanol over the normal catalyst, magnesium sulfate, during its irradiation with a beam of 800-kev electrons did not show any acceleration of the process. Thus, in this case the radioactive radiation of the solid is more effective than external irradiation of the solid.

Successful results have been obtained by the use of new radioactive catalysts. In 1960, Mikhailenko and Dobrosel'skaya studied the dehydration of n-dodecanol on tricalcium phosphate. The introduction of radioactive phosphorus P^{32} into the catalyst produced appreciable acceleration of the process at a specific radioactivity of the preparation of 27.6 mC/g (Fig. 8).

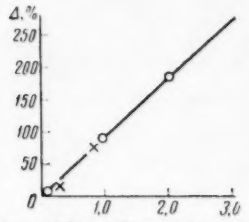

Fig. 7. Relation of the increase in the degree of conversion of cyclohexanol to the specific radioactivity of the catalyst (temperature 410°). The crosses refer to a catalyst with an initial activity of 105.2 mC/g after it had been stored for 188 and 314 days, respectively.

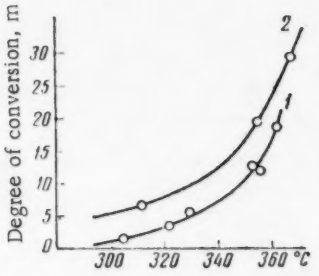

Fig. 8. Effect of the radioactivity of a tricalcium phosphate catalyst on the kinetics of n-dodecanol dehydration: 1) inactive catalyst; 2) radioactive catalyst containing P^{32} (27 mC/g).

It has also been established that radioactive radiation has an effect on the nature of the interaction of the solid phase and saturated solution in the case of sparingly soluble compounds. Spitsyn, Torchenkova, and Glazkova [11] studied the kinetics of the solution in water of barium sulfate containing various amounts of S^{35}. With preparations with a specific activity of 0.1-1.5 mC/g, there was first considerable supersaturation of the solutions, which was eliminated after the liquid had been stirred with the precipitate for approximately 25 hours. Precipitates of $Ba\overset{*}{S}O_4$ of higher activity (9-20 mC/g and above) did not show such a phenomenon: The concentration of SO_4^{2-} in them increased with time.

The kinetics of solution of a $Ba\overset{*}{S}O_4$ precipitate also depended on the method by which it was prepared. If the starting material was radioactive sodium sulfate, SO_4^{2-} ions were transferred into solution more rapidly and, after equilibrium had been reached, the calculated solubility of $Ba\overset{*}{S}O_4$ (20-40 mg/liter, 20°) was considerably greater than the value for barium sulfate (2.3 mg/liter, 18°). If the precipitates were prepared from labeled sulfuric acid, the solubility of $Ba\overset{*}{S}O_4$, measured from the concentration of SO_4^{2-} ions, was found to be much lower (4-6 mg/liter, 20°) though it still exceeded the solubility of inactive barium sulfate. It is interesting to note that in both cases the solubility of barium sulfate, containing various amounts of S^{35}, found had a maximum at a specific radioactivity of the preparation of the order of 1-1.5 mC/g (Fig. 9).

As another example, we may mention the solubility of cerium oxalate labeled with various amounts of Ce^{144} (half-life of 282 days), which was measured by Spitsyn and Moshchanskaya in 1960. Four samples of cerium oxalate with specific radioactivities of 0.008, 0.05, 0.5, and 4.3 mC/g were prepared under identical conditions. It was found that the solubility of cerium oxalate determined from the tracer Ce^{144} decreased with an increase in the specific activity. The composition of the solid phase was practically unchanged. As Fig. 10 shows, the solubility of cerium oxalate depended linearly on the logarithm of the specific radioactivity of the preparations. Extrapolation of the line to the abscissa axis for an infinitely low activity of the precipitate gives

a value for the solubility of cerium oxalate which is very close to that found by normal gravimetric and volumetric analysis methods. The stronger effect of the radioactive isotope on the solubility of cerium oxalate in comparison with $BaSO_4$ is probably explained by the high maximum energy of the radiation of Ce^{144} (0.348 Mev) and the short-lived daughter element Pr^{144} (2.97 Mev, half-life 17.5 minutes). The effect of the radiation of the radioactive tracer used on the solubility of sparingly soluble compounds should be considered when using tracer methods.

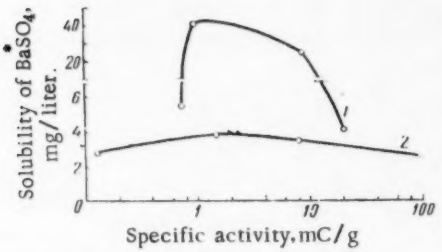

Fig. 9. Effect of specific radioactivity of $BaSO_4$ on its solubility in water at 20° (measured from the concentration of $\overset{*}{S}O_4^{2-}$). Methods of preparing $B\overset{*}{a}S\overset{*}{O}_4$: 1) $BaCl_2 + Na_2\overset{*}{S}O_4$; 2) $BaCl_2 + H_2\overset{*}{S}O_4$.

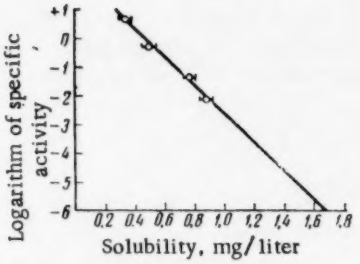

Fig. 10. Solubility in water of cerium oxalate of various specific activities at 25°.

The new experimental data presented in this report confirm the important effect of the radioactive radiation of solids on their physicochemical properties and on heterogeneous processes in which they are involved. It may be assumed that radiochemical activation of the surface of solids is of practical importance in adsorption and heterogeneous catalysis. However, it is necessary to carry out a large amount of research work to be able to choose the optimal materials for this application of radioactive substances.

SUMMARY

1. New data are presented on the effect of the radioactive radiation of S^{35} on the rate of isotopic exchange of sulfur at high temperature in the systems $K_2\overset{*}{S}O_4 - SO_3$ and $Na_2\overset{*}{S}O_4 - SO_3$ and of oxygen in the system $Na_2\overset{*}{S}O_4 - O_2^{18}$. External irradiation with high-energy electrons only affects the rate of isotopic exchange at higher doses than radioactive radiation.

2. Irradiation of barium sulfate with high-energy electrons and protons leads to a fall in its sorption powers with respect to organic dyes. The prolonged β-decay of S^{35} forming part of the sorbent has an analogous effect.

3. Potassium sulfate containing S^{35} has a higher sorption power for methanol vapor than inactive K_2SO_4.

4. New data are presented on the effect of added radioactive isotopes on the catalytic activity of catalysts.

5. Radioactive radiation affects the solution and solubility of sparingly soluble substances.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

DETERMINATION OF THE ENERGY OF THE BOND OF THE REACTING ATOMS OF ORGANIC MOLECULES WITH THE SURFACE OF MnO CATALYST

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Original article submitted January 14, 1959

Continuing an investigation [1, 2] of the conversion of alcohols over manganous oxide, we studied the kinetics of dehydration of trimethylcarbinol over this catalyst. The trimethylcarbinol we used had the following constants: b. p. 81.5-82° (750 mm); d^{20}_4 0.7885; $n^{20}D$ 1.3870. The experimental procedure and method of preparing the catalyst have been described previously [2]. Trimethylcarbinol was dehydrated in the temperature range 330 to 380°. The gaseous products consisted solely of unsaturated hydrocarbons. It was found that a considerable amount of isobutene dissolved in the catalyzate and therefore the amount of dissolved isobutene in the catalyzate was determined by the Kaufman – Vinogradova method for bromine numbers and an appropriate correction introduced into the calculations.

The rate constants of the reaction were calculated from the experimental values of the numbers of moles of substances reacting per unit time $\underline{m}$ by means of the general kinetic equation of monomolecular catalytic reactions in a flow system [3]:

$$[(\Sigma A_r + A_1\Sigma\nu_r) + P(z_rA_r + A_1\Sigma z_r\nu_r)]\ln\frac{A_1}{A_1 - m} - (\Sigma\nu_r + p\Sigma z_r\nu_r)m = Pksl. \quad (1) \qquad (1)$$

When applied to the dehydration of trimethylcarbinol

$$(CH_3)_3COH \longrightarrow (CH_3)_2C{=}CH_2 + H_2O,$$

where $z_1 = 1$; $\nu_1 = 1$; $\nu_2 = 1$; $\nu_3 = 1$; and P is large, the equation acquires the form

$$k = (z_2 + z_3)A_1\ln\frac{A_1}{A_1 - m} - (z_2 + z_3 - 1)m, \qquad (2)$$

where $\underline{k}$ is the rate constant of the reaction, $\underline{m}$ is the number of moles of substance reacting per unit of time (milliliters of unsaturated compounds separated per minute), A_1 is the number of moles of starting material introduced into the reactor per unit time (milliliters of gas at STP which would be formed by complete conversion of the starting material in 1 minute), and $\underline{z}$ gives the relative adsorption coefficients. The relative adsorption coefficients were determined from experiments with mixtures of the reacting substance and one of the reaction products. For the calculation, we used the formula [4]:

$$z = \frac{\frac{m_0}{m} - 1}{\frac{100}{p} - 1}, \qquad (3)$$

where m_0 is the number of milliliters of unsaturated compounds formed during the passage of the pure substance and $\underline{m}$ is the number of milliliters of unsaturated compounds formed during the passage of a mixture with a molar content $\underline{p}$.

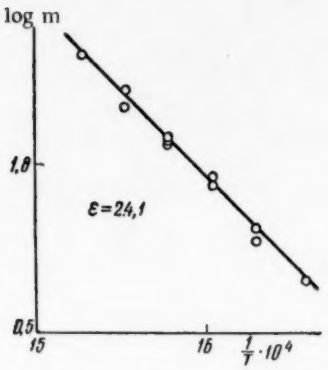


Fig. 1. Dehydration of trimethylcarbinol.

The first series of experiments was carried out to determine the apparent activation energy. The data from these experiments are given in Table 1 and Fig. 1. The activation energy was calculated by the Arrhenius equation from the relation of log m to 1/T and was found to equal 24.1 kcal/mole. Tables 2 and 3 give the results of experiments to determine the relative adsorption coefficients of isobutene and water. We could not exclude the possibility of partial oxidation of the manganous oxide under the experimental conditions with mixtures of alcohol and water, but prolonged regeneration of the catalyst (2-2.5 hours) always restored the initial activity of the catalyst. The determination of the relative adsorption coefficients and their temperature dependence made it possible to use a method given previously [5] to calculate the change in free energy ΔF, heat content ΔH, and entropy ΔS occurring during displacement of trimethylcarbinol by isobutene and water from the active centers of the catalyst:

$$\Delta F = -RT \ln z; \quad \Delta H = \frac{4{,}57\,(\lg z_1 - \lg z_2)}{\frac{1}{T_2} - \frac{1}{T_1}}; \quad \Delta S = \frac{\Delta H - \Delta F}{T}. \qquad (4)$$

The results obtained are given in Table 4. The true activation energy of trimethylcarbinol dehydration, calculated from the relation of log k to 1/T (ϵ = 31.0 kcal/mole), was found to be 6.9 kcal higher than the apparent activation energy (ϵ' = 24.1 kcal/mole).

TABLE 1

Dehydration of Trimethylcarbinol
(volume of MnO 16 ml; length of bed 8 cm; ΣA_r 63.7 ml/min; ϵ = 24.1 kcal/mole)

Temperature °C	m, ml/min	m, ml/min · ml of catalyst	lg k_0	$\frac{\epsilon}{\lg k_0}$	m calculated for ε = 24.1	Degree of conversion, %
360	12,0	0,750	8,200	2,94	0,740	18,84
380	20,8	1,300	8,189	2,94	1,313	32,64
330	4,5	0,281	8,199	2,94	0,278	7,06
350	8,7	0,544	8,196	2,94	0,542	13,67
340	6,0	0,375	8,184	2,94	0,384	9,42
360	11,7	0,731	8,189	2,94	0,740	18,37
370	15,1	0,944	8,174	2,95	0,986	23,70
340	6,4	0,400	8,212	2,93	0,384	10,05
370	15,9	0,994	8,197	2,94	0,986	25,00
350	9,1	0,569	8,215	2,93	0,542	14,30
360	11,3	0,706	8,174	2,95	0,740	17,74

* k_0 is the pre-exponential term in the Arrhenius equation.

TABLE 2

Relative Adsorption Coefficients of Isobutene
(Trimethylcarbinol – isobutene mixtures)

Amt. of alcohol in mixture, mol.%	m	z	Amt. of alcohol in mixture, mol. %	m	z	Amt. of alcohol in mixture, mol. %	m	z
Temperature 380°			Temperature 370°			Temperatu re 360°		
100	20,8		100	15,9		100	12,5	
64	12,3	1,23	64	8,0	1,76	64	4,9	2,73
39	7,3	1,19	39	4,2	1,79	39	2,3	2,84
100	20,8		100	15,9		100	12,5	
64	12,2	1,25	64	8,5	1,55	64	4,9	2,73
39	7,4	1,16	64	8,1	1,71	39	2,3	2,84
100	20,8		39	4,1	1,84			
64	7,3	1,19						
		z_{av}=1,20			z_{av}=1,73			z_{av}=2,78

TABLE 3

Relative Adsorption Coefficients of Water
(Trimethylcarbinol – water mixtures)

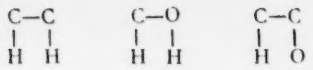
Amt. of alcohol in mixture, mol. %	m	z	Amt. of alcohol in mixture, mol. %	m	z
Temperature 380°			Temperature 360°		
100	20,8		100	12,5	
85,5	11,1	5,17	85,5	7,1	4,50
53	3,9	4,90	53	2,3	4,98
100	20,8		100	12,5	
85,5	11,2	5,09	85,5	7,2	4,32
53	3,8	5,06	53	2,3	4,98
		z_{av}=5,05			z_{av}=4,70

TABLE 4

Thermodynamic Functions

Temperature, °C	ΔH, cal/mole	ΔF, cal/mole	ΔS, cal/deg · mole
Trimethylcarbinol – isobutene			
360	– 32,700	– 1285	– 49.6
370	– 32,700	– 700	
380	– 32,700	– 236	– 49.7
Trimethylcarbinol – water			
360	2018	– 1949	6.27
380	2018	– 2097	6.31

We previously studied the kinetics of isopropanol, cyclohexanol, and cyclohexene dehydrogenation on manganous oxide [2]. The kinetics of trimethylcarbinol dehydration were studied in this work. This made it possible to use a known method [6] to determine the energies of the bonds of the reacting atoms with the catalyst surface. The indices of these reactions are as follows:



(I) (II) (III)

where I is for the dehydrogenation of hydrocarbons, II the dehydrogenation of alcohols, and III the dehydration of alcohols. The energy barriers for these reactions when the reaction is limited by adsorption are as follows:

$$\begin{aligned} E_1 &= -2Q_{C-H} + 2Q_{C-C} + 2Q_{H-C} \\ E_2 &= -Q_{C-H} - Q_{C-O} + Q_{C-C} + Q_{O-C} + 2Q_{H-C} \\ E_3 &= -Q_{C-H} - Q_{O-C} + 2Q_{C-C} + Q_{H-C} + Q_{O-C} \end{aligned} \qquad (5)$$

Considering the data of Kondrat'ev [7] on bond energies in organic molecules ($Q_{C-H} = 98.7$ and $Q_{C-O} = 85.5$ in kcal) and also the relation $\epsilon = -\frac{3}{4}E$, by solving the system of Eqs. (5) we obtained:

$$\begin{aligned} Q_{HC} &= \frac{1}{3}(-\varepsilon_1 - 2\varepsilon_2 + 2\varepsilon_3) + 62 \\ Q_{CC} &= \frac{1}{3}(-\varepsilon_1 + 2\varepsilon_2 - 2\varepsilon_3) + 45{,}1 \\ Q_{OC} &= \frac{1}{3}(3\varepsilon_1 - 2\varepsilon_2 - 2\varepsilon_3) + 48{,}6 \end{aligned} \qquad (6)$$

The activation energy of cyclohexane dehydrogenation $\epsilon_1 = 32.0$ (due to the low degree of conversion of about 4%, the true and apparent activation energies are similar in this case). The true activation energy of isopropanol dehydrogenation $\epsilon_2 = 31.9$, and the true activation energy of trimethylcarbinol dehydration $\epsilon_3 = 31.0$. With these data, the energies of the bonds of the reacting atoms with the catalyst surface equal: $Q_{H-C} = 50.75$, $Q_{C-C} = 26.7$ and $Q_{O-C} = 38.8$. If we use the bond energies in organic molecules according to Cottrell's data [8], then the values of Q_{H-C} and Q_{O-C} are unchanged, while Q_{C-C} is decreased by 8.3 kcal.

SUMMARY

1. The kinetics of trimethylcarbinol dehydration on manganous oxide were studied. The relative adsorption coefficients of water and isobutene and their temperature dependence were determined. The thermodynamic functions of the catalytically active surface were calculated.

2. The energies of the bonds of the reacting atoms of the organic molecule with the catalyst surface were determined by a kinetic method.

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CHANGE IN CATALYTIC ACTIVITY OF NICKEL STEARATE DURING THE OXIDATION OF ETHYLBENZENE

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The catalytic action of metal salts in chain oxidations of hydrocarbons is usually connected with the additional formation of radicals by reaction of the metal salt with hydroperoxide. Due to the rapid reaction between the metal salt and hydroperoxide, the maximum concentration of the latter in the catalyzed reaction is found to be much lower than in an uncatalyzed reaction. This has been observed in many experimental works. However, in the liquid-phase oxidation of a number of hydrocarbons catalyzed by nickel stearate $NiSt_2$, we observed that the maximum concentration of hydroperoxide is found to be approximately equal to its concentration in the uncatalyzed reaction. The present work was devoted to the investigation of this phenomenon. It was shown that the anomalous course of the kinetic curve for hydroperoxide in the oxidation of ethylbenzene is associated with deactivation of the catalyst during the oxidation.

EXPERIMENTAL

Separate experiments were carried out on the oxidation of n-decane, but the bulk of the investigation was devoted to the oxidation of ethylbenzene. As Figs. 1 and 2 show, the amount of hydroperoxide formed in the presence of nickel stearate practically coincided with that observed in uncatalyzed reactions. In particular, it is interesting that the concentration of hydroperoxide with catalysis by nickel stearate was almost 100 times more than in catalysis by cobalt stearate. Since it may be considered that in the presence of $NiSt_2$, initiation of chains may proceed not only through the reaction of $NiSt_2$ with hydroperoxide, but also through the reaction with one of the oxidation products, we checked the possibility of a direct reaction between $NiSt_2$ and the oxidation products, namely, alcohol and acetophenone. The possibility of such a mechanism has been pointed out in the literature, for example, in the work of Bawn, et al. [1], who showed that in the catalytic oxidation of benzaldehyde, the initiation of chains by the reaction

$$Co^{+++} + C_6H_5C(=O)H \longrightarrow Co^{++} + H^+ + C_6H_5C(=O)\cdot$$

proceeds much more rapidly than by the reaction:

$$Co^{+++} + C_6H_5C(=O)OOH \longrightarrow Co^{++} + H^+ + C_6H_5C(=O)OO\cdot .$$

In these experiments, $NiSt_2$ (0.01 mole/liter) was introduced into a solution of ethylphenylcarbinol, benzyl alcohol, or acetophenone in ethylbenzene (0.02 mole/liter). The solution obtained was kept at 120° for 5 hours in the absence of oxygen. When the solution had been cooled, we determined the alcohol or acetophenone content, depending on which of the products was used for the experiment. No change in the concentration of alcohol or ketone was detected in the experiments, i.e., they did not react with the catalyst.

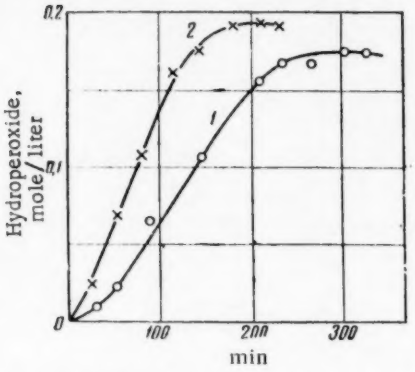

Fig. 1. Kinetics of hydroperoxide accumulation during the oxidation of n-decane at 144°: 1) without catalyst; 2) in the presence of nickel stearate, 0.014 mmole/ml.

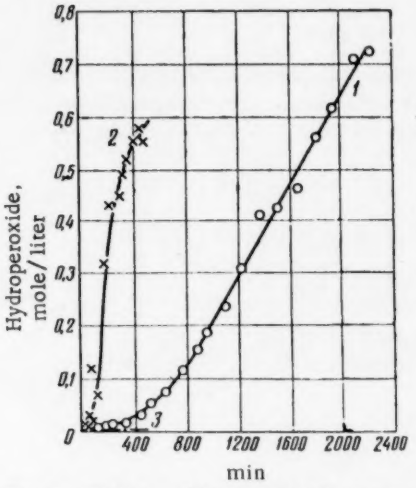

Fig. 2. Kinetics of hydroperoxide accumulation during the oxidation of ethylbenzene at 120°: 1) without catalyst; 2) in the presence of nickel stearate, 0.016 mmole/ml; 3) in the presence of cobalt stearate, 0.017 mmole/ml.

In other experiments, we compared the catalytic activity of the initial catalyst with the activity of a catalyst which had been in the reacting system for a definite time. The rate constant of catalytic decomposition of ethylbenzene hydroperoxide was taken as a measure of the catalytic activity. The results of two typical experiments are shown graphically in Fig. 3. In one of these experiments, ethylbenzene was oxidized in the presence of $NiSt_2$ at 120° for 260 minutes. The mixture was then cooled to room temperature rapidly and nitrogen (free from oxygen) passed through the mixture for 30 minutes to remove dissolved oxygen. The mixture was then reheated to 120° and samples removed from the reaction vessel periodically for peroxide determination.

A second experiment was carried out in exactly the same way as the first but before the oxidate was reheated, a sample of fresh catalyst was introduced into the reaction vessel. As Fig. 3 shows, in the second experiment the rate of peroxide decomposition was many times greater than in the first. This meant that $NiSt_2$ loses practically all its catalytic activity during the course of the oxidation. This fall in the activity of the catalyst is evidently associated with the accumulation of products which react with the catalyst. The existence of such products is also indicated by experiments in which we measured the relation of the rate of catalytic decomposition of ethylbenzene hydroperoxide W to the initial hydroperoxide concentration $(ROOH)_0$. The corresponding semilogarithmic representations of the kinetic curves are given in Fig. 4. As this figure shows, a very unusual phenomenon was observed in these experiments. The decomposition rate constant $\underline{k}$ fell with an increase in $(ROOH)_0$, though within the limits of each experiment, the decomposition obeyed the first order law and the rate constant remained unchanged to the end of the reaction. This relation of $\underline{k}$ to $(ROOH)_0$ was obtained not for pure hydroperoxide, but for the oxidate.

For a qualitative explanation of the observed effect, let us assume that the oxidate contains a substance X which forms an inactive complex with nickel stearate $NiSt_2 \cdot X$. As follows from experiments in which the decomposition of peroxide with various initial concentrations of $NiSt_2$ was studied and also from experiments on the decomposition of peroxide (Fig. 4), $W = k\,(NiSt_2) \cdot (ROOH)$, where (ROOH) is the concentration of hydro-

peroxide. In the presence of the substance X, part of the $NiSt_2$ is bound in a complex and the concentration of $NiSt_2$

$$(NiSt_2) = [(NiSt_2)_0 - (NiSt_2 \cdot X)] = \frac{(NiSt_2 \cdot X)}{K[(X_0) - (NiSt_2 \cdot X)]};$$

where K is the equilibrium constant of the complex-formation reaction and the indices "0" refer to the initial concentrations.

We prepared solutions with different initial concentrations of peroxide by dilution of the oxidate with pure ethylbenzene. Therefore, the value $X_0 = \alpha(ROOH)_0$, where α is a constant. Considering this relation and substituting the value of $(NiSt_2)$ in the expression for W, we have:

$$W = \left\{k \frac{(NiSt_2 \cdot X)}{K[\alpha(ROOH)_0 - (NiSt_2 \cdot X)]}\right\}(ROOH),$$

where the curly brackets close the empirical rate constant of peroxide decomposition. From the relation obtained it follows that the empirical rate constant increases with a decrease in $(ROOH)_0$. Thus, the observed dependence of the decomposition rate constant on the initial concentration may be explained by the presence in the oxidate of a product which deactivates the catalyst.

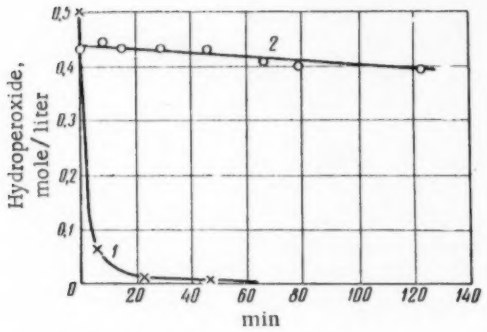

Fig. 3. Kinetics of hydroperoxide decomposition in hydrocarbon oxidized for 260 minutes at 120°: 1) with the addition of fresh catalyst, 0.016 mmole/ml; 2) without the addition of catalyst.

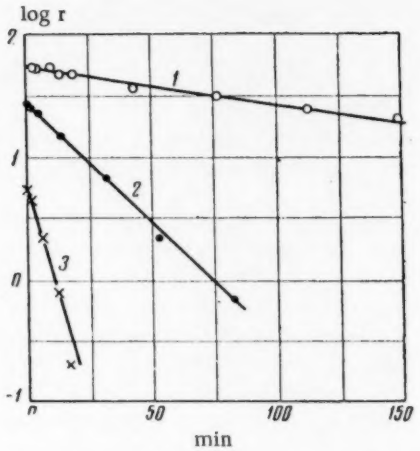

Fig. 4. Semilogarithmic plots of the kinetic curves of hydroperoxide decomposition at 120°; the catalyst was 0.008 mmole/ml of nickel stearate; initial hydroperoxide concentrations: 1) 0.54 mmole/ml; 2) 0.27 mmole/ml; 3) 0.054 mmole/ml.

In each given experiment on hydroperoxide decomposition, the rate constant remains unchanged during the process. This means that the products of hydroperoxide decomposition, namely, alcohol and ketone, hardly change the activity of the catalyst. At the same time, as is shown by the above, in the presence of oxygen when there is further oxidation of the decomposition products, the activity of the catalyst falls during the process. Since acids accumulate in the system as a result of the oxidation of peroxide decomposition products, it may be assumed that it is precisely the acids which deactivate the catalyst, for example, by formation of insoluble salts [2-4].

In connection with this hypothesis, we carried out experiments in which the kinetics of the loss of activity by the catalyst were compared with the kinetics of the accumulation of acids. A small part of each of the samples taken during the reaction was analyzed for acid content; a large part was evaporated in vacuum to

constant weight at 45°. The catalyst powders obtained were dissolved in oxidate containing peroxide and the kinetics of peroxide decomposition measured in a nitrogen atmosphere at 120°. The activity of the catalyst could be assessed from the rate constant of peroxide decomposition. The curves obtained for the change in activity of the catalyst during the course of the reaction and the kinetic curves of acid accumulation are illustrated in Fig. 5. The fact that the curves were completely symbatic indicates that the fall in the activity of the catalyst was associated with its reaction with acids.

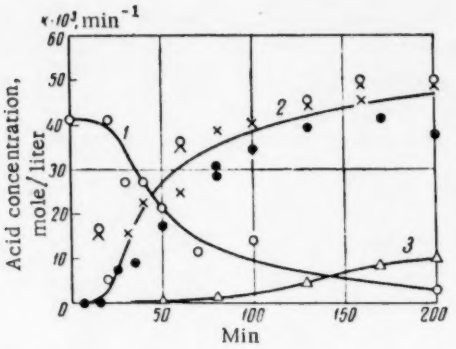

Fig. 5. Relation of catalyst activity to degree of reaction: 1) change in catalyst activity during reaction; 2) kinetic curve of acid accumulation; 3) kinetic curve of the accumulation of water-soluble acids at 120°. Nickel stearate – 0.0043 mmole/ml.

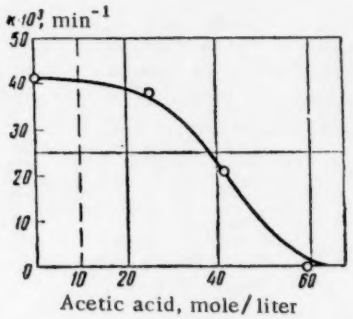

Fig. 6. Relation of catalyst activity to acetic acid content of ethylbenzene at 120°. Nickel stearate – – 0.0043 mmole/ml.

It should be noted that in the systems studied, the exchange reaction between free acid and salt is extremely complex. This is indicated by experiments with the addition of acetic or benzoic acids to the solution of hydroperoxide and $NiSt_2$ in ethylbenzene. A sample of $NiSt_2$ and acid was introduced into ethylbenzene. The mixture was kept at 120° in the absence of oxygen for 2 hours for an exchange reaction to occur between the salt and the acid. The solution was then cooled, hydroperoxide added to it, nitrogen passed for 30 minutes, the solution again heated to 120°, and the kinetics of peroxide decomposition measured at this temperature. As Fig. 6 shows, acetic acid almost completely deactivated the catalyst. Reduction of the catalyst activity by a factor of 10, for example, required 5-6 times as much acid as for the same reduction in activity in the oxidation reaction itself. In the presence of benzoic acid, catalytic decomposition of hydroperoxide began at a considerably higher rate than without the addition of acid, but the decomposition rate fell rapidly during the reaction and became considerably less than the rate in the absence of additive.

The fall in catalyst activity during the reaction, which we established, makes it possible to understand the course of the curve of peroxide accumulation in reactions catalyzed by nickel stearate (see Figs. 1 and 2). During the time in which the maximum peroxide concentration is reached, the nickel salt is completely deactivated. The reaction, therefore, proceeds by a noncatalytic mechanism and the maximum peroxide concentrations practically coincide. In addition, the maximum concentration is reached more rapidly in the presence of nickel stearate since the latter has a strong catalytic action in the initial stages of the reaction.

The results of this work again indicate that, strictly speaking, metal salts are not catalysts but initiators in the catalytic oxidation of hydrocarbons; their activity and often the mechanism of their action change during the process. For this reason, the observed kinetics of the reaction reflect not only the properties of the reacting system, but also the change in activity and function of the catalyst in different stages of the chemical conversion. As a result, the analysis of the chemical rules is extremely complicated. In investigations of the catalysis mechanism, particular attention should be paid to the stabilization of the catalyst. Stabilization of the catalyst apparently would considerably simplify work on the elucidation of the mechanism of the catalytic action of metal salts.

SUMMARY

1. In the oxidation of ethylbenzene catalyzed by nickel stearate, the activity of the catalyst gradually falls as a result of reaction of nickel stearate with acids formed during the oxidation.

2. The anomalous course of the kinetic curve of hydroperoxide accumulation during the catalyzed reaction is associated with deactivation of the catalyst.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

MACROSCOPIC STAGES IN THE OXIDATION OF PROPANE IN THE PRESENCE OF CHLORINE

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Investigation of the heat evolution by the reaction mixture during exothermal reactions is a very effective method of studying the kinetics and mechanism of complex chain reactions. In particular, this method has made it possible to demonstrate the presence of two macroscopic stages, separate in time, in the hydrogen bromide-catalyzed oxidation of propane to acetone [1], isobutane to tert-butyl hydroperoxide [2], and ethane to acetic acid [3], and also in the oxidation of propane in the presence of NO_2 [4]. Two heat-evolution maxima were obtained by Urizko and Polyakov [5] and also by Enikolopov and Konareva [6] in the investigation of methane oxidation by oxygen with the addition of nitrogen oxides. Enikolopov and Konareva considered that the first of these maxima was caused by the reaction of NO_2 with methane and the second by the oxidation of methane initiated by the intermediate product formed in the first-stage; they also obtained two heat-evolution maxima when chlorine, bromine, HCl and HBr were added to the methane – oxygen mixture.

Our previous work on the oxidation of propane in the presence of chlorine gave grounds for proposing that in this case there is an initial macroscopic initiated stage, which then initiates the main oxidation of propane. In actual fact, a study of heat evolution of the reaction mixture during the process showed the presence of two macroscopic stages (two heat-evolution conditions) in the reaction mechanism. In the present work, it is shown that this result may be interpreted by considering that two branched chain reactions may occur in the system.

EXPERIMENTAL

The oxidation of propane was studied by measuring the heat evolution of the mixture during the process on the usual static apparatus with a quartz reaction vessel (d = 30 mm) with a differential thermocouple (copper – constantan with a wire diameter of 0.05 mm), enclosed in a capillary (d = 0.4 mm). One junction of the thermocouple was at the center of the vessel, half way along it, and the other was at the wall of the reaction vessel. This thermocouple made it possible to measure the temperature difference between the reaction mixture in the center of the vessel and that at the wall. The pressure in the vessel was measured with a membrane gauge. Figure 1 gives curves of the heat-evolution rate and kinetic curves of the pressure change at 340 and 358° for a stoichiometric mixture of propane and oxygen at P_{init} = 244 mm Hg. The heat-evolution maximum for 340° equalled ΔT_m = 5.15 cm on the scale (or 3.1°) and for 358°, ΔT_m = 8.4 cm on the scale (or 4.90°).

The linear nature of the semilogarithmic plots of the initial sections of curves of Δp against t, which are also given in Fig. 1, indicates that Semenov's law for the initial period of branched chain reactions $\Delta P \approx Ae^{\varphi t}$ is obeyed quite well. We previously obtained the same law for the kinetic curves of aldehyde formation when the reaction was carried out under flow conditions. Since the over-all rate of heat evolution is proportional to the rate of the chemical reaction,

$$\Delta T_m = \frac{QR^2W}{4\lambda \cdot 760 \cdot 22\,400} \frac{273}{T_i}.$$

then it is quite natural that the amount of heating of the reaction mixture corresponds to the inflection on the kinetic curve of pressure change.

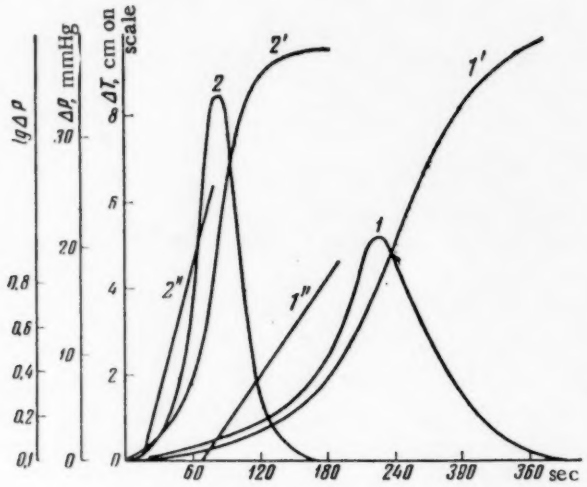

Fig. 1. Temperature dependence of the heat-evolution rate (1, 2) and pressure change (1', 2') for the mixture $C_3H_8 + O_2$; P_{init} = 244 mm Hg. We also give logarithmic plots of the pressure change curves (1", 2"). 1, 1', 1") for 340°; 2, 2', 2") for 358°.

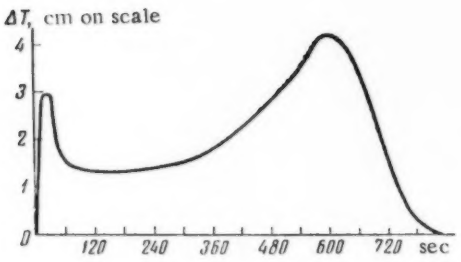

Fig. 2. Curve of the heat-evolution rate for the mixture $C_3H_8 + O_2 +$ 2% Cl_2 at P_{init} = 478 mm Hg and T = 327°.

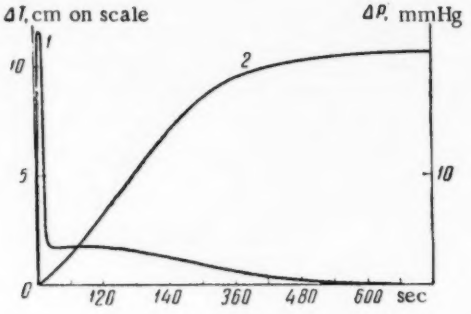

Fig. 3. Curves of heat-evolution rates (1) and pressure change (2) for the mixture $C_3H_8 + O_2 +$ + 8% Cl_2 at P_{init} = 244 mm Hg and T = 340°.

The character of the heat evolution changed substantially when small amounts of chlorine were introduced into the system. The curve of the change in the heating of the mixture for a reaction in the presence of chlorine (2% by volume), which is given in Fig. 2, has two characteristic maxima at 327°. The first maximum was reached 25 seconds after the beginning of the reaction and was 2.9 cm on the scale (or 1.76°) in size, while the second was reached after 600 seconds and was 4.2 cm on the scale (or 2.55°) in size. The presence of the two maxima indicates the existence of two macroscopic stages.

Figures 3, 4, and 5 give curves of the change in heating and kinetic curves of the pressure change with various amounts of chlorine added and at various temperatures. It is readily seen that the size of the maxima and their ratio are strongly affected by the experimental conditions (temperature, pressure, and amount of chlorine added).

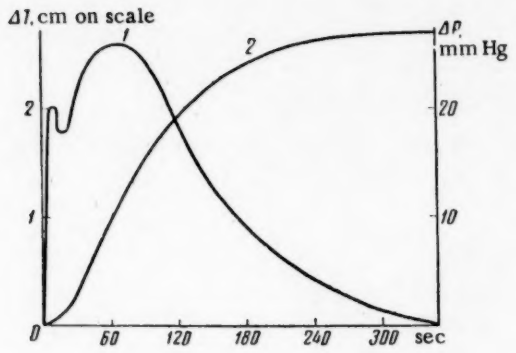

Fig. 4. Curves of heat-evolution rate (1) and pressure change (2) for the mixture $C_3H_8 + O_2 +$ + 3.5% Cl_2 at P_{init} = 244 mm Hg and T = 358°.

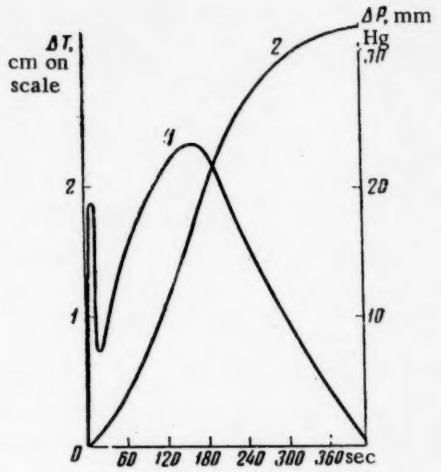

Fig. 5. Curves of heat-evolution rate (1) and pressure change (2) for the mixture $C_3H_8 + O_2 +$ 8% Cl_2 at P_{init} = 244 mm Hg and T = 372°.

In [6] an examination was made of variants of two-stage processes from the point of view of the nature of the corresponding heat-evolution curves, and it was emphasized that there will be two heat evolution maxima if both stages have an autocatalytic character.

In our case, we attempted to explain the presence of two heat-evolution maxima by the occurrence of two degenerate branched reactions in the system. In this case, a product formed as a result of the first stage causes degenerate branching in the second stage. Calculation for the proposed scheme actually makes it possible to obtain two maxima on the calculated heat-evolution curve, analogous to those which we observed experimentally. In the general schematic form, the reaction mechanism may be represented in the following way:

$$B + R \rightarrow C + R \quad (1)$$

$$C \rightarrow 2R \quad (2)$$

$$A + R' \rightarrow D + Q' \quad (3)$$

$$D + C \rightarrow 2R' \quad (4)$$

$$R \rightarrow \text{— Destruction} \quad (5)$$

$$R' \rightarrow \text{— Destruction} \quad (6)$$

where B is the initiating additive, A is the starting material, R and C are the free radical and final product of the first stage, and R' and D are the free radical and final product of the second stage. Reactions 2 and 4 are the branching reactions, which involve the intermediate product C formed as a result of the first macroscopic stage. Chain termination is effected by the destruction of radicals by reactions 5 and 6. We assume that there is linear chain termination with a destruction of radicals on the wall of the reaction vessel.

The radical formation rates W_0 and W'_0 play an essential part in the initial period, changing the induction period. Branching is more important in a reaction that has already developed. To simplify the calculation, we will therefore consider the process at some time $t = t_1$, measured from the beginning of the reaction when it is possible to neglect the chain initiation rates W_0 and W'_0. It is not difficult to write differential equations for the rates of formation of all the products:

$$\frac{dR}{dt} = W_0 + 2k_2C - k_5R \approx 2k_2C - k_5R$$

$$\frac{dC}{dt} = k_1BR - k_2C - k_4DC \approx k_1BR - k_4DC$$

$$\frac{dB}{dt} = -k_1BR \qquad \frac{dD}{dt} = a_3R' - k_4DC \approx a_3R'$$

$$\frac{dR'}{dt} = W'_0 - k_6R' + 2k_4DC \approx 2k_4DC - k_6R',$$

where $a_1 k_1A$; $a_3 = k_3A$.

By neglecting the values W_0 and W'_0, assuming stationary concentrations of active centers and neglecting the consumption of D and C in degenerate branching, we obtain:

$$R = 2\frac{k_2}{k_5}C \qquad R' = 2\frac{k_4}{k_6}CD$$

$$\frac{dB}{dt} = -2k_1B\frac{k_2}{k_5}C = -2\frac{k_1k_2}{k_5}BC; \quad C = -\frac{dB}{dt}\frac{k_5}{2k_1k_2B}$$

$$\frac{dD}{dt} = a_3R' = 2\frac{a_3k_4}{k_6}DC = \frac{2a_3k_4}{k_6}D\left(-\frac{dB}{dt}\frac{k_5}{2k_1k_2B}\right) = -\frac{D}{B}\frac{dB}{dt}\alpha,$$

where

$$\alpha = \frac{a_3k_4k_5}{k_6k_1k_2}$$

From $\frac{dD}{D} = -\frac{dB}{B}\alpha$ we find that: $D = D_0\left(\frac{B_0}{B}\right)^{\alpha}$. By substituting this value in $\frac{dC}{dt} = \frac{dB}{dt}\left(\frac{D_0B_0^{\alpha}}{B^{\alpha+1}}\beta - 1\right)$,

where $\beta = \frac{k_4k_5}{2k_1k_2}$, we obtain:

$$dC = dB\left(\frac{D_0B_0^{\alpha}}{B^{\alpha+1}}\beta - 1\right).$$

Integration of this equation with the condition that when $C = C_0$, $B = B_0$, gives:

$$C = B_0 + C_0 + \frac{D_0\beta}{\alpha} - B - \frac{D_0B_0^{\alpha}}{\alpha B^{\alpha}}\beta.$$

By substituting the value found in the equation for $\frac{dB}{dt}$, we find:

$$\frac{dB}{dt} = -k_1BR = -2\frac{k_1k_2}{k_5}BC = -\gamma BC, \text{ where } \gamma = \frac{2k_1k_2}{k_5}$$

$$\int_{B_0}^{B} \frac{dB}{-\gamma B\left(B_0 + C_0 + \frac{D_0\beta}{\alpha} - B - \frac{D_0 B_{0i}^{\alpha}\beta}{\alpha B^{\alpha}}\right)} = \int_{t_0}^{t} dt.$$

To solve this integral by numerical integration, it is necessary to determine the values of the constants in the constant values of the expression under the integral: k_1, k_2, α_3, k_4, k_5, k_6. We adopted a value of the constant of the bimolecular reaction of a radical with a molecule k_1 of the order of 10^{-18} cm^3/molecules·sec, bearing in mind the fact that the activation energy for the reaction of a radical with a molecule is less than 10 kcal/mole [7]. The constant k_2 (for monomolecular decomposition) was estimated from the time of the first stage (15 seconds):

$$k_2 = \frac{\ln 2}{t_{1/2}} = \frac{0{,}69}{7{,}5} = 0{,}9 \cdot 10^{-1} \text{ sec}^{-1}.$$

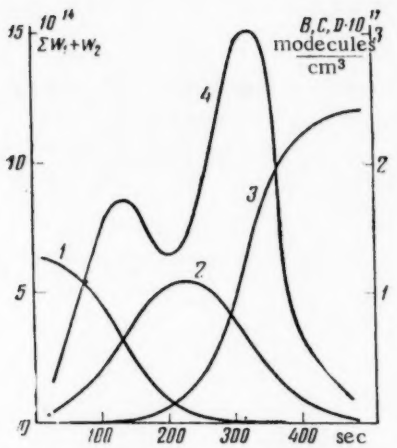

Fig. 6. Calculated curves for the formation and consumption of products B (1), C (2), and D (3) and heat evolution (4).

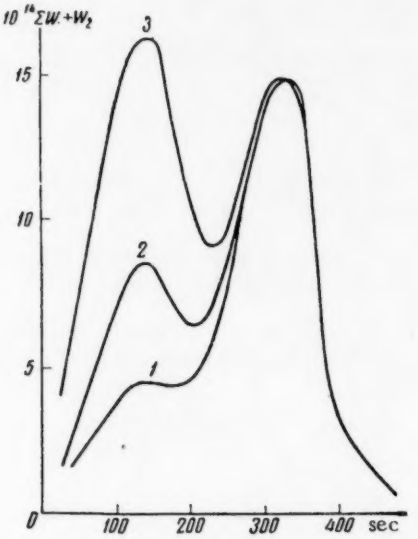

Fig. 7. Curves of the heat-evolution rate for a low ratio of thermal effects of the 1st and 2nd stages: 1) 0.5 $W_1 + W_2$; 2) $W_1 + W_2$; 3) $2W_1 + W_2$.

By taking the concentration [A] = $1.8 \cdot 10^{18}$ molecules/cm^3 from experimental data and adopting the constant $k_3 = 0.5 \cdot 10^{-18}$ cm^3/molecules·sec, we found that $\alpha_3 = k_3$ [A] = 0.91 sec^{-1}. The constant of the bimolecular reaction of the final product with the intermediate was estimated from the time of the second stage (400 sec) by the formula: $k_4 = \frac{1}{t_{1/2} \cdot c}$. By using the value $c = 0.15 \cdot 10^{17}$ molecules/cm^3, we found that $k_4 = 10^{-19}$ cm^3/molecules·sec. The values of k_5 and k_6 (linear termination constants) were taken to be the same and equal to 1 sec^{-1}. Then:

$$\alpha = \frac{\alpha_3 k_4 k_5}{k_6 k_1 k_2} = 1 \quad \beta = \frac{k_4 k_5}{2k_1 k_2} = 0{,}55 \quad \gamma = \frac{2k_1 k_2}{k_5} = 18 \cdot 10^{-20} \frac{\text{cc}}{\text{molecule} \cdot \text{sec}}$$

By using these data to solve the integral, we obtained kinetic curves for B, C, and D (Fig. 6). Figure 6 shows that the kinetic curve of the product of the first stage passes through a maximum as the product B is consumed. Product D of the second stage is formed from the moment of formation of C and reaches the maximum amount when all substance C is consumed. It is obvious that a "halt" in the reaction, which has been observed repeatedly in oxidation reactions, occurs as a result of the consumption of all the intermediate product. The amount of heat evolution is proportional to the reaction rate. For our case:

$$\Delta T_m = k(Q_1 W_1 + Q_2 W_2),$$

where Q_1 and Q_2 are the heat effects of the first and second stages;

$$W_1 = -\frac{dB}{dt}; \qquad W_2 = \frac{dD}{dt}; \qquad k = \frac{R^2}{4\lambda},$$

where R is the radius of the reaction vessel and λ is the mean thermal conductivity of the reacting gases (cal/cm · sec · deg). Figure 6 gives kinetic curves of the formation of products C and D and of the consumption of B and the curve of the change in $W_1 + W_2$ with time for the case when $Q_1 = Q_2$. It is evident that the two heat-evolution maxima are analogous to those which were obtained experimentally. The sizes of the maxima vary over a wide range, depending on the ratio of Q_1 and Q_2 (Fig. 7).

The authors would like to thank D. G. Knorre for discussing the work.

SUMMARY

1. The oxidation of propane by oxygen in the presence of chlorine at various temperatures (327, 340, 358, and 372°) was studied by measuring the heating of the mixture during the reaction.

2. When chlorine was introduced into the system $C_3H_8 + O_2$, two heat-evolution maxima were clearly observed and these indicated that there are two macroscopic stages, separate in time, in the reaction mechanism.

3. By calculation, it was shown that two heat-evolution maxima may be obtained when there occur two degenerate branched stages in which a product of the first stage produces degenerate branching of the chain in the second stage.

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MEASUREMENT OF IGNITION LAGS AT HIGH TEMPERATURES

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Shock waves with their almost instantaneous change in temperature and pressure may be used as a convenient initiator of fast high-temperature reactions in the gas phase; this explains their wide use in the study of the kinetics of these reactions. For example, the high temperatures of the gas in shock waves make it possible to produce ignition of fuel – oxidant mixtures and study its kinetics under conditions close in temperature to the conditions existing in flames.

An important characteristic of the rate of a chemical reaction is the ignition lag and this is readily determined experimentally as the time from the beginning of heating of the mixture in the shock wave to ignition. The ignition lags for $H_2 - O_2$ and C_3H_8 – air mixtures at various temperatures have been measured previously [1, 2]. We undertook to determine the ignition lags of a series of hydrocarbon – air mixtures at various temperatures and compare them. In the present work, we describe the method we used for studying the temperature dependence of ignition lags and preliminary experimental results.

EXPERIMENTAL

As ignition by shock waves reflected from a rigid wall is more stable than ignition in an incident wave and occurs in a stationary gas, which is very convenient for investigation by means of transducers, we carried out all experiments with reflected waves. The apparatus was a tube 6 m long with an internal diameter of 50 mm and consisted of three parts (Fig. 1): part 1 was filled with a normal mixture of $CH_4 + 2O_2$ (or another detonating mixture) at an initial pressure from 1 to 4 atm, part 2 was filled with an unreactive mixture of gases with the same acoustic impedance as the fuel – oxidant mixture, which was present in the working chamber 3 (for mixtures of a small amount of fuel and air, part 2 was filled with air). The acoustic impedances had to be the same to prevent reflection of the wave from the boundary between the buffer gas and the mixture investigated. Sections 1 and 2 were separated by a membrane 15 and sections 2 and 3 were separated by a tap 4 with a through hole of the same diameter as the tube; the tap was opened immediately before an experiment after gas had been passed into sections 2 and 3. Gas was passed into chambers 2 and 3 at the same pressure. The mixtures were made up either in rubber bags with the components measured with a GSB-400 gas meter and with manual mixing or in a metal tank with the components measured by pressure and mixing by diffusion for 2 days. On either side of the end of the working chamber were windows of transparent plastic. Opposite one of the windows on the outside of the tube was fixed an IFP-200 pulse discharge tube and opposite the other window was a photorecorder, focused on the inner surface of the window farthest from it. On the end plate was fixed a piezo-quartz pressure transducer and a two-electrode ionization gauge, whose circuit is shown in Fig. 1.

The mixture in chamber 1 was ignited with an ignition plug, the detonation wave shattered the membrane and decayed, and there passed through the inert gas a shock wave, which entered the working chamber and ignited the mixture on reflection. The intensity of the incident wave was regulated by the initial pressure in chamber 1. A graph of the relation of the Mach number of the shock wave to the pressure in chamber 1 is shown

in Fig. 2. When passing the piezo-quartz transducer 6, the wave produced a pulse, which was fed into an amplifying system and through a time lag circuit and fired the discharge tube 9 so that it gave off light at the moment that the shock wave was passing windows 7 and 8. The plastic surface on which the photorecorder was focused was coated with a thin layer of an aqueous solution of gelatin before the experiment. Under the action of the pressure in the shock wave, the gelatin became turbid and a shadow representation of the track left by the shock wave on the gelatin was obtained with the photorecorder. The light emitting process in the tube was photographed on the same plate and the intensity of the tube discharge was chosen so that it did not distort the representation of the process. At the same time, the ionization current from gauge 11 was recorded on the OK-17 M oscillograph, which was started by transducer 10.

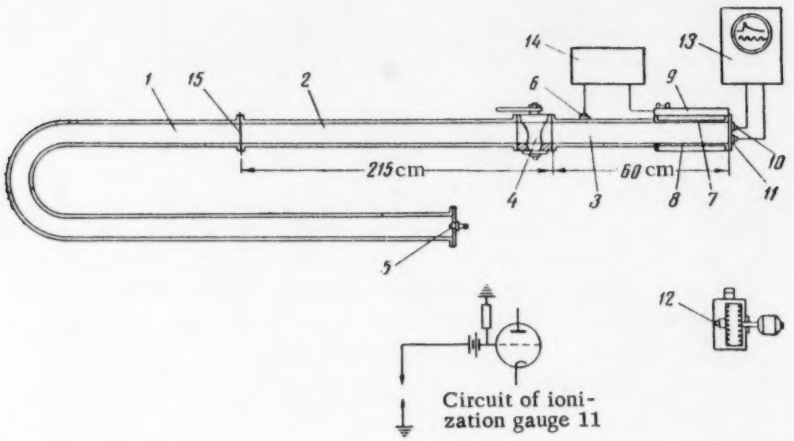

Fig. 1. Plan of apparatus: 1) chamber with initiator; 2) buffer chamber; 3) working chamber; 4) tap; 5) ignition plug; 6, 10) pressure transducers; 7, 8) windows; 9) IFP-200 tube; 11) ionization gauge; 12) photorecorder; 13) oscillograph; 14) time lag circuit; 15) membrane.

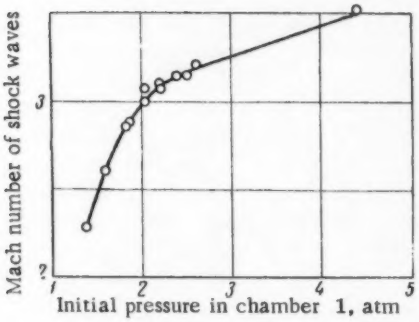

Fig. 2. Relation between the ratio of the shock wave velocity to the velocity of sound and the initial pressure in chamber 1 (the gas in chamber 1 was $CH_4 + 2O_2$ and the gas in chamber 3 was 3% C_6H_6 + 97% air).

To be sure that the peak of the shock wave was sufficiently planar so that the temperature and pressure of the gas hardly changed from the moment of arrival of the wave at the end to the moment of ignition, we carried out experiments with shock waves in air. Had the shock wave had a triangular form, then the velocity of the incident wave would have fallen with distance to the end, while the velocity of the reflected wave in the laboratory system of coordinates would have increased with distance from the end. Analysis of the photographs showed that neither the rate of the reflected wave nor that of the incident wave changed appreciably with distance (over a time of $\leq 10^{-3}$ sec). The velocity of the gas after the wave, determined from the slope of the light band on the photographs (Fig. 3,a), which was the track of the motion of the detonation products from chamber 1, was somewhat greater than the velocity of the gas after the wave, calculated from the measured velocity of the incident shock wave. The mean ratio of the gas density in the reflected wave to the initial density, measured as the ratio of the distance from the membrane to the end to the distance from the point at which the detonation products from chamber 1 encountered the reflected wave to the end, was somewhat greater than the value calculated from the velocity of the incident wave. This may be explained by intense mixing of the detonation products and the buffer gas at the boundary. It is probable, with

times from the moment of reflection close to 10^{-3} sec, cooling of the gas by the rarefaction wave begins to have an effect, as ignition is very unstable with ignition lags of this value.

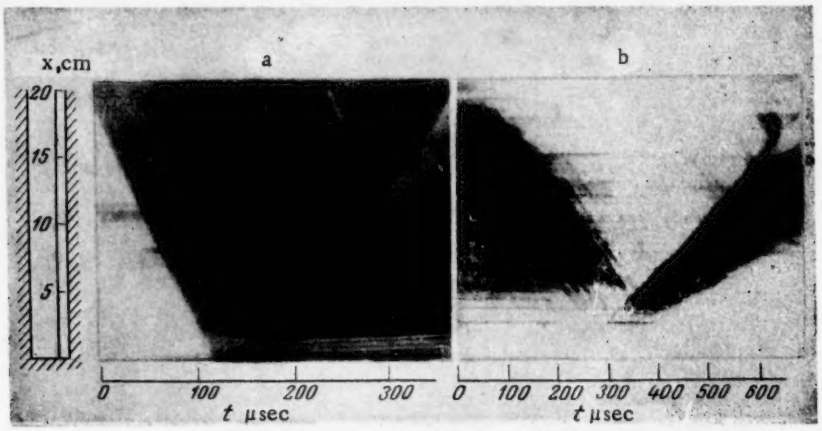

Fig. 3. Time scan of shock wave motion. The plastic was coated with gelatin (a) and carbon black (b).

Fig. 4. Time scan of shock wave motion and ignition process. The ionization current pulse is given at the bottom of the photograph. The time marks are 100 kc.

To obtain a trace of the shock wave, we tried replacing gelatin by other materials (various types of oil, BF-6 glue, and carbon black); they all gave positive results, but the clearest photographs were obtained with gelatin and the next best was carbon black (Fig. 3, b). The use of carbon black was convenient in that the photograph showed the motion of the carbon black, whose velocity was close to the velocity of the gas after the shock wave. Thus, on an apparatus designed for comparatively low static pressures, in gas initially at atmospheric pressure we obtained shock waves with a Mach number ≤ 4 with a peak which could be regarded as planar (motion after the wave was uniform and stationary) at least for a period of $\leq 10^{-3}$ sec. The Mach number of the shock wave could be varied over a wide range by changing the pressure in chamber 1. The procedure for obtaining a picture of the motion of the shock waves was very simple. The apparatus required hardly any adjustment and occupied little space. The drawback of the gelatin solution is the fact that it dries out very rapidly; dry gelatin did not record the shock wave. Carbon black is free from this drawback, but it did not give such a clear trace of the shock wave. It should be noted that a clear illustration of the trace of the shock wave on photographs was obtained for waves, the pressure in whose front was more than 3 atm.

Calculation of gas temperature. The gas temperature in the reflected shock wave was calculated from the velocity of the incident wave with allowance for the temperature dependence of the heat capacity of the gas. From tables of enthalpy at various temperatures [3], we found the ratio ρ_0/ρ in the incident wave from the formula

$$\rho_0/\rho = -\beta + \frac{\theta - 1}{2} + \sqrt{\left(\frac{\theta - 1}{2} - \beta\right)^2 + \theta}.$$

We then determined the relation of the value $\alpha = \frac{\mu D^2}{RT_0} = \frac{2\beta}{1 - \left(\frac{\rho_0}{\rho}\right)^2}$ to ρ_0/ρ.

For finding the temperature in the reflected wave, the values of β and θ from tables were substituted in the formula

$$\alpha = \frac{\beta_1}{1 - \frac{\rho_0}{\rho}} - \frac{\theta_1}{1 - \frac{\rho_0}{\rho}\frac{\theta_1 - 1}{\beta_1}}.$$

Since the relation of α to ρ_0/ρ is known, from the last formula, we can find α or the velocity of the incident shock wave, heating the gas to the temperature θ_1 on reflection. The following symbols were adopted in the formulas: T_0 and ρ_0 are the initial temperature and density of the mixture, μ is the mean molecular weight, D is the velocity of the incident wave, T and ρ are the temperature and density after the incident wave, T_1 is the temperature after the reflected wave, H(T) is the heat content of 1 g of mixture; $\theta = \frac{T}{T_0}$; $\theta_1 = \frac{T_1}{T_0}$; $\beta = \frac{\mu [H(T) - H(T_0)]}{RT_0}$; $\beta_1 = \frac{\mu [H(T_1) - H(T_0)]}{RT_0}$; for gas mixtures $\beta = \Sigma \alpha_i \beta_i$, where α_i is the volume fraction of a mixture component and β_i is the dimensionless enthalpy of the i-th gas.

The ignition lag depends strongly on the extent to which the reactions occurring before ignition are adiabatic. We estimated the heat loss from the heated gas to the walls and toward the shock wave leaving the end. After a time $t \leq 10^{-3}$, these losses were very small and so they could be neglected.

Experimental results. Figure 4 gives a time scan of the ignition of a mixture of 2% C_7H_{16} + 98% air. The photographs were similar for other mixtures. The incident wave moved from top to bottom and the time increased from right to left. The ionization pulse on the oscillograph is given at the bottom of the photograph; the time marks had a frequency of 100 kc. As can be seen, the ignition began from the end plate and a detonation wave then spread with a Mach number in the range of 2.5-3.5. With high ignition lags (10^{-4} - 10^{-3} sec), ignition did not essentially begin at the end and its position changed from experiment to experiment. In this case, the reaction began at a point inside the tube and spread as a flame with a velocity of approximately 100 m/sec, which accelerated and then there was detonation.

The velocity of the reflected shock wave hardly changed during the ignition lag and its measured value was always greater than the value calculated from the velocity of the incident wave by 50-70 m/sec.

Figure 4 shows that the ionization current between the electrodes on the end plate increased sharply at the moment of ignition and then began to fall. The maximum current corresponded to that calculated by Sahas equation [4] at the explosion temperature without allowance for impurities with a low ionization potential. A comparison of photographs of the ionization current pulses with photographs of the ignition process obtained on the photorecorder showed that the moment of the appearance of intense light emission coincided with the moment of the appearance of the ionization current.

The reaction rate at the moment of explosion was very great as the rate of increase in the ionization current corresponded to a rate of increase in temperature of approximately 10^{9}° K/sec. The fall in ionization after the maximum is explained by cooling of the reaction products as a result of their expansion. In the case of ignition by a reflected shock wave, the time during which the gas temperature increased was determined by the ignition lag. The ignition lags obtained (τ) and the calculated temperatures in the reflected shock wave (T) were plotted in the coordinates of log τ against 1/T. Figure 5 gives the results of experiments with a mixture of 10% CH_4 and 90% air at an initial pressure in the tube of 1 atm. The points lay about a straight line corresponding to a pre-exponent of 10^{-4} and an activation energy of 60.5 kcal/mole. For a mixture of

2% C_7H_{16} and 98% air, $\tau = 10^{-10} e^{\frac{16100}{T}}$; for a mixture of 3% C_6H_6 and 97% air, $\tau = 10^{-13.6} e^{\frac{26200}{T}}$; and for a mixture of 3.5% C_4H_{10} and 96.5% air, $\tau = 10^{-11.9} e^{\frac{20200}{T}}$ (all the relations are for an initial pressure in the tube of 1 atm).

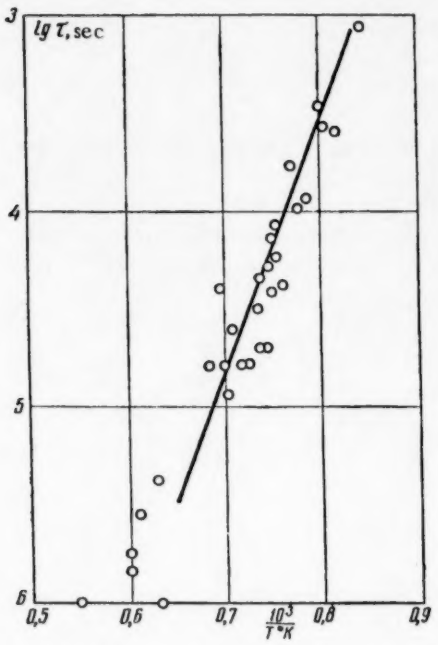

Fig. 5. Relation of logarithm of ignition lag to reciprocal temperature in the reflected wave (initial pressure in tube 1 atm).

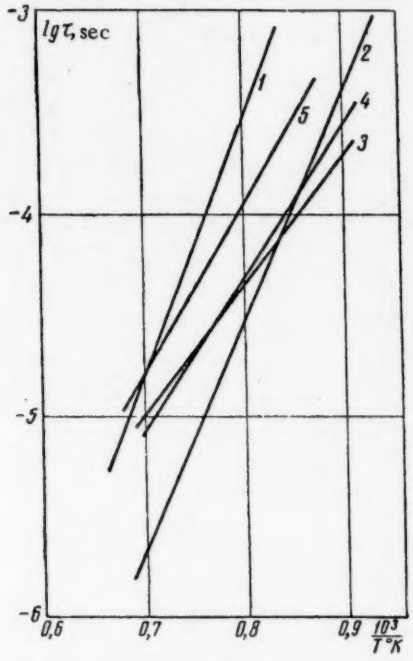

Fig. 6. Relation of logarithm of ignition lag to reciprocal temperature: 1-4) lines we obtained with the initial pressure in chamber 3 atmospheric; 5) taken from [1] with an initial pressure of 300-100 mm Hg: 1) mixture of 10% CH_4 + 90% air; 2) mixture of 3% C_6H_6 + 97% air; 3) mixture of 2% C_7H_{16} + 98% air; 4) mixture of 3.5% C_4H_{10} + 96.5% air; 5) mixture of 3.9% C_3H_8 + 96.1% air.

A comparison of experiments with a mixture of 10% CH_4 + 90% air with an initial pressure in the tube of 1 and 0.16 atm showed that the pressure dependence of the ignition lag is quite substantial: A decrease in the pressure at which the reaction began by a factor of 6.3 increased the ignition lag by a factor of 60. As all the experiments were carried out at a constant initial pressure in the tube, with an increase in temperature, there was an increase in the pressure at which the reaction began. With an initial pressure in the tube of 1 atm, the pressure in the reflected wave increased from approximately 50 atm at 1100° K to approximately 90 atm at 1500° K. Thus, the activation energies we determined from the slope of the lines of log τ against $1/T$ were somewhat high and the pre-exponents low. For a mixture of 2% n-C_7H_{16} + 98% air, we obtained the temperature dependence of the ignition lag at constant pressure. The initial pressure of the mixture in the tube in this case was chosen so that, with reflection of waves of different intensity from the wall, the pressure of the reflection was constant and equaled 55 atm. For the ignition lags we obtained the equation $\tau = 19^{-9} e^{\frac{13900}{T}}$ instead of the equation given above $\tau = 10^{-10} e^{\frac{16100}{T}}$, which was obtained with a constant initial pressure in the tube. The relation of ignition lag to pressure was not calculated for other mixtures.

Figure 6 gives a comparison in the coordinates of log τ against $1/T$ of lines from experimental points for different mixtures. Stoichiometric mixtures of paraffins from CH_4 to C_7H_{16} have almost the same ignition lags ($\leq 10^{-5}$ sec) at temperatures of $\geq 1500°$ K. For temperatures $\geq 1200°$K, mixtures of propane, butane, and heptane have longer ignition lags at the same temperatures than a mixture of benzene and air.

SUMMARY

1. The temperature dependences of the lag in ignition by shock waves for mixtures of a series of hydrocarbons with air were determined.

2. The degree of ionization of the gas during explosion was equilibrium, i.e., corresponded to that calculated by the Sahas equation.

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THEORY OF CHAIN-THERMAL FLAME PROPAGATION

COMMUNICATION 3. EFFECT OF TRANSFER COEFFICIENTS ON THE FLAME PROPAGATION RATE

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In one of the first articles [1] we examined the effect of thermal conductivity and diffusion coefficients on the flame propagation rate with a theoretical relation obtained for a system with a simplified chain reaction scheme and one type of active center [2]. Instead of the absolute values of the flame propagation rates, we determined their ratios for mixtures with different diffusion coefficients for the active centers and different thermal conductivities. Numerical calculations for three stoichiometric methane – oxygen mixtures diluted with nitrogen (methane – air mixture), argon instead of nitrogen ("argon" air) or helium instead of nitrogen ("helium" air) showed that the ratio of the flame propagation rates for these three mixtures, calculated from the theoretical relations [1, 2], agreed with the experimental ratio. These calculations were carried out for a change in the diffusion coefficients of one of the possible active centers, and therefore could not lead to results which agreed closely with experiment as no allowance was made for the simultaneous change in the diffusion coefficients of hydroxyl and hydrogen atoms.

In a previous article [3], relations were derived for determining the flame propagation rate in a system with an unbranched chain reaction, including two active centers with different diffusion coefficients. This made it possible to refine the theoretical value calculated previously [1] for the ratio of the flame propagation rates for the three methane – oxygen mixtures diluted with nitrogen, argon, and helium, respectively.

Calculated relations. In [3] we obtained the following relation for determining the flame propagation rate in a system with an unbranched chain reaction including two active centers:

$$u_0 = \varphi\xi\psi\varphi_D \frac{1}{2\rho_0} \sqrt{(n_{1r}D_{1m}+n_{2r}D_{2m})\,K_m}\,, \tag{1}$$

where

$$\varphi = 2\sqrt{\frac{2q}{\varkappa}\left(1-\frac{2q}{\varkappa}\right)}, \tag{2}$$

$$\varphi_D = \sqrt{\frac{(n_{1r}D_{1m}+n_{2r}D_{2m})(G_{1m}+G_{2m})}{(n_{1r}+n_{2r})(G_{1m}D_{2m}+G_{2m}D_{1m})}}\,, \tag{3}$$

$$K_m = \frac{2}{cT_r}\,\frac{(S_{1m}G_{2m}+S_{2m}G_{1m})}{(G_{1m}+G_{2m})}\,, \tag{4}$$

and the other values are determined by the relations:

$$\frac{2q}{\varkappa} = \frac{2q_1q_2(n_{1r}+n_{2r})}{n_{1r}\varkappa_1 q_1 + n_{2r}\varkappa_2 q_2},\quad D_1 = \rho D_{P_1},\ D_2 = \rho D_{P_2},$$

$$\varkappa_1 = \frac{cD_{10}}{\lambda_0},\quad \varkappa_2 = \frac{cD_{20}}{\lambda_0},\quad D_{10} = D_{1m}q_1,\ D_{20} = D_{2m}q_2,$$

$$q_1 = \frac{\mu_0}{\mu_m}\left(\frac{T'_0}{T'_m}\right)^{a_1-1} \text{ when } D_{P1}\sim(T')^{a_1},\quad q_2 = \frac{\mu_0}{\mu_m}\left(\frac{T'_0}{T'_m}\right)^{a_2-1},$$

$$\text{when } D_{P2}\sim(T')^{a_2},\quad T = T' - T'_0,\ T_m = 0{,}5T_r,\ G_1 = F_1 + F_4,$$

$$G_2 = F_2 + F_3,\ S_1 = h_1F_1 + h_4F_4 \text{ и } S_2 = h_2F_2 + h_3F_3.$$

The index "0" refers to the initial state of the fresh mixture ($T = T'_0$), the index "Г" to the state at the combustion temperature ($T' = T'_Г$), and the index "m" to the state corresponding to the maximum temperature gradient (at $T' = T'_m$). In the relations presented, n_1 and n_2 are the concentrations of active centers (mole/g of mixture), D_{P_1} and D_{P_2} are the diffusion coefficients of the active centers (cm^2/sec), λ is the thermal conductivity (cal/cm·sec·deg), $\underline{c}$ is the heat capacity at constant pressure (cal/g·deg), T is the temperature in °K, ρ is the density (g/cm^3), h_i is the heat effect of the chain propagation reaction (cal/mole), F_i is the product of the rate constant of chain propagation K_i (g^2/cm^3·mole·sec) and the concentration of the corresponding starting material (mole/g of mixture), which is represented as a function of temperature [2, 3]; ξ and ψ are coefficients allowing for the effect of the rate of initiation and the rate of quadratic termination of chains, respectively, which are determined by the relations presented in [3].

It was shown previously [1, 2, 3] that allowance for the rates of chain initiation and quadratic termination does not have a substantial effect on the theoretical value of the flame propagation rate in systems with unbranched chain reactions or in systems with branched reactions when the rate of the branching process is relatively small in comparison with the rate of the chain propagation process. An exception to this rule may be the case when special substances (for example, ozone) which decompose readily with the formation of active centers, are added to the combustion mixture. In examining the combustion of hydrocarbons without any special additives, it may be assumed that $\xi = 1$ and $\psi = 1$ with a high degree of accuracy.

Without knowing the chain reaction scheme of methane oxidation, it is impossible to calculate the absolute theoretical values of the flame propagation rate from relation (1) and consequently, the accurate theoretical ratio of the flame propagation rates for the three given cases. However, with some simplifications, it is possible to calculate approximately the theoretical ratio of the flame propagation rates. Without knowing the absolute values of G_{1m} and G_{2m}, it is impossible to calculate the accurate values of the coefficients φ_D (3) and it is necessary to assume that the ratio of the coefficients φ_D for the two mixtures containing inert gases as diluents equals unity. This assumption would be completely correct with the rate constants of the chain propagation reaction independent of the properties of the inert diluent if the diffusion coefficients of the active centers changed in the same ratio on replacement of the inert diluent in the hot mixture. In actual fact, as is shown by the data presented in the article of Clingman, Brokaw, and Pease [4], replacement of argon by helium, for example, leads to an increase in the diffusion coefficient of hydroxyl by a factor of 2, while the diffusion coefficient of hydrogen atoms increases by a factor of only 1.5 (Table 1).

Without knowing the absolute values of G_{1m} and G_{2m}, it is necessary to represent the value K_m as the effective rate constant of chain propagation [2, 3] for which the absolute value is unknown, but for which we known only the temperature dependence, determined from the relation of the flame propagation rate to the pressure in the methane – oxygen mixtures [5]. This temperature dependence of K_m is presented in [1].

Assuming that the temperature dependences of the diffusion coefficients of the active centers are the same ($a_1 = a_2 = a$) and considering that $K_m = K'_m \rho^2_m$ [3], where $\rho_m = \rho_0 \frac{\mu_m}{\mu_0}\frac{T'_0}{T'_m}$ and μ is the molecular weight of the mixture, and that the partial pressure of the corresponding active center at the combustion

temperature P_{ir} is related to the concentration n_{ir} (mole/g of mixture) by the relation $P_{ir} = n_{ir} \rho_m 82.06 T'_m$, we obtained from (1) a relation for determining the ratio of the flame propagation rates

$$\frac{(u_0)_L}{(u_0)_N} = \frac{\varphi_L(\varphi_D)_L}{\varphi_N(\varphi_D)_N} \sqrt{\frac{(P_{1r}D_{P10} + P_{2r}D_{P20})_L}{(P_{1r}D_{P10} + P_{2r}D_{P20})_N}} \sqrt{\frac{(K'_m)_L}{(K'_m)_N}} A_T, \quad (5)$$

where

$$A_T = \left(\frac{\mu_{mL}\mu_{0L}}{\mu_{0N}\mu_{mN}}\right)\left(\frac{T'_{0L}}{T'_{0N}}\right)^{\frac{2-a}{2}}\left(\frac{T'_{mN}}{T'_{mL}}\right)^{\frac{3-a}{2}},$$

and the indices "N" and "L" denote values in the first and second (new) states, respectively.

TABLE 1

Starting Data for Three Stoichiometric Combustion Mixtures (with 9.46% methane) taken from [4]

Inert diluent		Nitrogen	Argon	Helium
Combustion temperature, °K		2214	2514	2514
Partial pressures, atm · 10^4	H	3,57	26,1	26,1
	OH	27,8	100,4	100,4
	O	2,11	19,5	19,5
Diffusion coefficients at T'_0 = 298°K, cm^2/sec	H	0,969	0,987	1,49
	OH	0,246	0,240	0,476
	O	0,273	0,268	0,531
Thermal conductivity of mixture at 0°C, $\lambda \cdot 10^5$, cal/cm · sec · · deg		5,99	4,71	19,5

Numerical calculations. We used relation (5) for numerical calculations of the ratios of the flame propagation rates in three stoichiometric methane – oxygen mixtures (9.46% methane), diluted with nitrogen (stoichiometric methane – air mixture), argon instead of nitrogen (stoichiometric mixture of methane with "argon" air), or helium instead of nitrogen (stoichiometric mixture of methane with "helium" air).

Table 1 gives the starting data required for calculations from relation (5), which were taken from the work of Clingman, Brokaw, and Pease [4].

For all mixtures, it was assumed that $\mu_0 = \mu_m$ and $a_1 = a_2 = a = 1.9$. The temperature dependence of the effective rate constant of flame propagation K'_m was taken from [1]. It was considered that the value of K'_m did not change on replacement of the inert diluent and depended only on temperature. The experimental ratio of the flame propagation rates for the three given mixtures was taken from [4] (Table 2). The flame propagation rate in a methane – oxygen mixture with argon was taken as unity in Table 2. In addition to the results of calculation from relation (5), Table 2 gives corresponding data obtained from the thermal theory and also results of a calculation according to the diffusion theory of Tanford and Pease from [4]. For comparison, Table 2 gives the theoretical ratios of the flame propagation rates obtained for a system with a simplified chain reaction scheme and one type of active center [1]. In these calculations, it was assumed that flame propagation was determined by the diffusion of hydrogen atoms alone or the diffusion of hydroxyl alone.

The calculation from relation (5), the results of which are given in the last line in Table 2, made allowance for the concentrations of hydrogen atoms and hydroxyl. The concentration of oxygen atoms was neglected due to the relatively low concentration of oxygen in comparison with the concentration of hydroxyl when they have approximately equal diffusion coefficients (Table 1).

TABLE 2

Experimental and Theoretical Ratios of the Flame Propagation Rates in Methane – Oxygen Mixtures (with 9.46 % methane) Diluted with Nitrogen (Air Mixture), Argon, or Helium

Source	$(u_0)_{N_2}$	$(u_0)_A$	$(u_0)_{He}$
Experimental data [4]	0,43	1	1,42
From the thermal theory [4]		1	2,03
From the theory of Tanford and Pease [4]	0,36	1	1,32
Considering only hydrogen atoms [1]	0,31	1	1,77
Considering only hydroxyl [1]	0,43	1	0,91
From relation (5) with allowance for H and OH	0,40	1	1,41

SUMMARY

1. A relation determining the dependence of the flame propagation rate on the diffusion coefficients of the active centers and the thermal conductivity of the combustion mixture was obtained and used for calculating the theoretical ratio of the flame propagation rates in three different stoichiometric methane – oxygen mixtures.

2. The theoretical ratios of the flame propagation rates are in good agreement with the corresponding ratios determined experimentally.

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POTENTIALS OF Pt AND Au ELECTRODES IN HNO_3 AND $NaNO_3$ SOLUTIONS UNDER THE ACTION OF IONIZING RADIATION

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Under the action of ionizing radiation, the potential of an electrode immersed in a dilute aqueous solution undergoes definite shifts as a result of processes caused by the radiolysis of water. If the primary radiolysis products of water (H, OH, H_2, H_2O_2) react readily with the dissolved substance, oxidizing or reducing it, and there arises an equilibrium system, the electrode potential corresponds to the ratio of the activities of the oxidized and reduced forms. A typical example is a solution of ferrous and ferric salts. As we showed previously, during the irradiation of solutions of ferrous salts in sulfuric or perchloric acid, the potential of a Pt electrode passes through all the values of the equilibrium potential, corresponding to the ratios $(Fe^{3+})/(Fe^{2+})$, established as a result of radiation oxidation of Fe^{2+} ions [1].

Under conditions where the solution does not contain substances undergoing oxidation or reduction, as was shown by Veselovskii et al. [2, 3], the primary radiolysis products may react directly with the electrodes, creating a definite potential, which depends on the nature of the electrode. Thus, during the irradiation of nitrogen-saturated solutions of H_2SO_4 and NaOH, at a Pt electrode there was established a stationary potential close to the hydrogen potential and, at a Au electrode, a potential which was strongly displaced toward the oxygen potential. The authors explained these effects by the selective reaction of the Pt electrode with the reducing and the Au electrode with the oxidizing components of water radiolysis.

In systems with intermediate properties such as solutions of nitric acid and nitrates, the picture is more complex. Before reaching a stationary value, the potential of the Pt electrode is displaced in positive and negative directions. The nature and magnitude of these displacements, like the value of the stationary potential, depend on the concentration of the solution and its acidity [4]. Despite their complex nature, the changes in potential in irradiated solutions are quite reproducible. The present work was undertaken to elucidate the processes determining these effects. Pt and Au electrodes were compared and a study was made of the effect of the composition of the nitrate solutions and the dose strength on the change in potential.

EXPERIMENTAL

The radiation source was a BFV-70 short-focus sealed x-ray tube, operating at 50 kv and 20-200 ma. The solution was irradiated and the potential measured as described previously in a cell with a rotating electrode and a thin bottom, through which the beam passed in an upward direction [1]. The volume of liquid irradiated was 10 cc. The dose strength was varied in different experiments from $2.6 \cdot 10^{15}$ to $3.1 \cdot 10^{16}$ ev/cm^3·sec; it was determined from the oxidation of $FeSO_4$ in 0.8 N H_2SO_4, with the assumption that $G(Fe^{3+}) = 15.5$. The potential was measured at room temperature relative to a calomel electrode and then converted to the value relative to a normal hydrogen electrode.

The solutions were made up in water that was distilled twice after prolonged treatment with $KMnO_4$. Chemically pure grade sodium nitrate was recrystallized twice from doubly distilled water. The irradiation was carried out with a solution saturated with oxygen-free nitrogen [5]. The gas was passed through the solution for 1-1.5 hours before irradiation and during the whole experiment at a constant rate of approximately 10 cm^3/min.

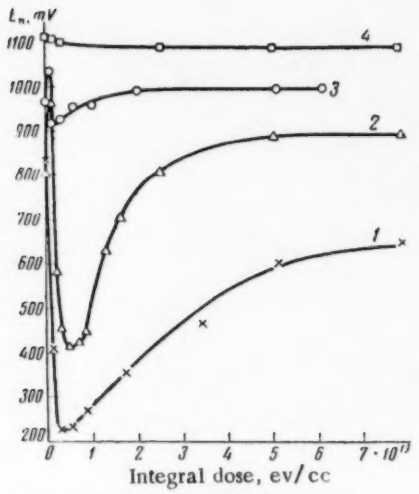

Fig. 1. Potential of Pt electrode in irradiated HNO_3 solutions: 1) 0.05 M; 2) 0.5 M; 3) 1 M; 4) 4 M (dose strength d. s. = $3.1 \cdot 10^{16}$ ev/$cm^3 \cdot$ sec).

The platinum electrode was treated with boiling nitric acid, washed with water, and then kept in the solution until there was established the potential characteristic of each solution and lying within the range of E_H = 800 mv to E_H = 1100 mv in 0.05 to 4 M HNO_3 solution and within the range of approximately 600-700 mv in 0.05-4 M $NaNO_3$ solution. Where necessary, the electrode was "adjusted" to the standard starting value by alternate cathode and anode polarization. The gold electrode was treated with boiling hydrochloric acid and then in the same way as the platinum electrode. The standard starting potentials differed little from those presented above for the Pt electrode.

Experimental results. The changes in potential during the irradiation of 0.05, 0.5, 1, and 4 M HNO_3 solutions are given in Fig. 1 for a platinum electrode and in Fig. 2 for a gold electrode.* These data were obtained at a dose strength of $3.1 \cdot 10^{16}$ ev/$cm^3 \cdot$ sec. In contrast to the Au electrode, the Pt electrode showed a sharp displacement of the potential in a negative direction at the beginning of irradiation. As the HNO_3 concentration was increased, this displacement decreased and disappeared completely in 4 M solution, in which the course of the change in potential of the two electrodes was the same. The potential of the Au electrode depended little on the HNO_3 concentration. In both cases, after the absorption of a certain amount of energy, a potential was established which did not change with further irradiation.

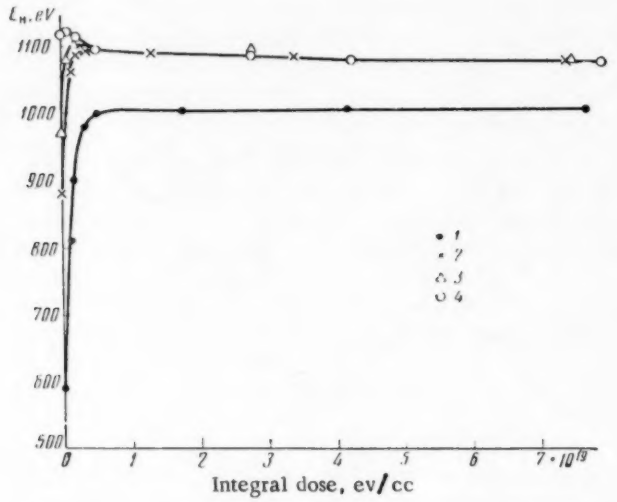

Fig. 2. Potential of Au electrode in irradiated HNO_3 solutions: 1) 0.05 M; 2) 0.5 M; 3) 1 M; 4) 4 M; d. s. = $3.1 \cdot 10^{16}$ ev/$cm^3 \cdot$ sec.

* The positive sign corresponds to oxidizing potentials.

The potential of both electrodes was quite stable. After brief anode or cathode polarization during irradiation, it rapidly returned to the value before polarization. After the radiation had been stopped, the potential was displaced and after a few minutes it acquired a new stationary value, which was also stable and was retained after anode or cathode polarization. Figure 3 gives the change in the potential of the Au electrode in 1 M HNO_3 solution during irradiation (solid line) and after it had stopped (broken line); moments of brief anode and cathode polarization are indicated by the letters A and C on the curve. The potential of the Au electrode in HNO_3 solutions was always displaced in a negative direction after irradiation stopped.

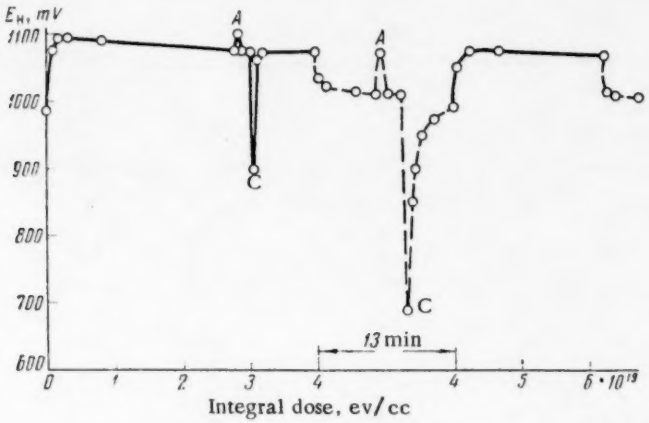

Fig. 3. Potential of Au electrode in 1 M HNO_3: —— during irradiation, d. s. = $3.1 \cdot 10^{16}$ ev/cm^3 · sec; - - - - - after irradiation stopped.

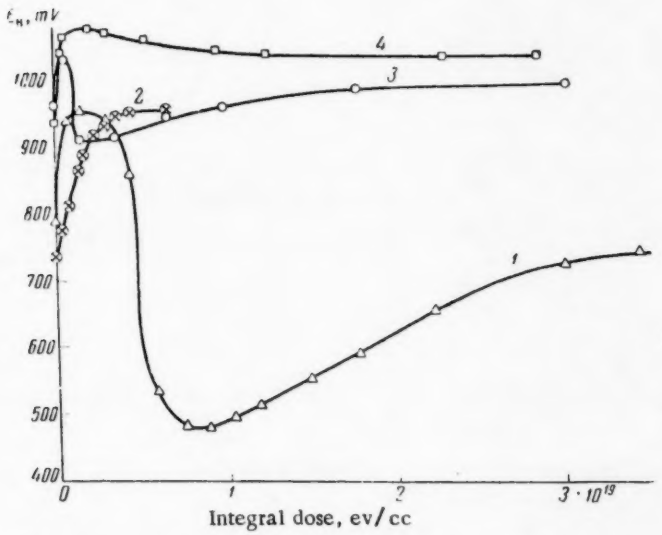

Fig. 4. Potential of Pt electrode in 0.5 and 1 M HNO_3 at various dose strengths: 1) 0.5 M HNO_3, d. s. = $2.6 \cdot 10^{16}$ ev/cm^3 · sec; 2) 0.5 M HNO_3, d. s. = $2.6 \cdot 10^{15}$ ev/cm^3 · sec; 3) 1 M HNO_3, d. s. = $3.1 \cdot 10^{16}$ ev/cm^3 · sec; 4) 1 M HNO_3, d. s. = $3.1 \cdot 10^{15}$ ev/cm^3 · sec.

For each concentration, the course of the change in the Pt-electrode potential depended on the dose strength. As is shown in Fig. 4, a fall from $3.1 \cdot 10^{16}$ to $3.1 \cdot 10^{15}$ ev/cm^3 · sec and from $2.6 \cdot 10^{16}$ to $2.6 \cdot 10^{15}$ ev/cm^3 · sec led to the disappearance of the minimum from the curves obtained in 1 and 0.5 M HNO_3. With a fall in the dose strength to $3.1 \cdot 10^{15}$ ev/cm^3 · sec, the potential of the Au electrode in 1 M HNO_3 became approximately 50 ev less positive. In this case, the potentials of the two electrodes coincided both during irradiation and after it had stopped, as is shown by Fig. 5. In neutral $NaNO_3$ solutions there were analogous changes in the potentials of platinum and gold electrodes during irradiation. Figures 6 and 7 give curves for

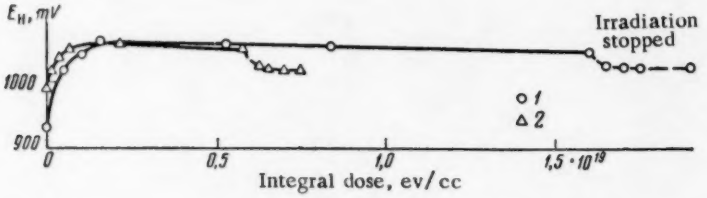

Fig. 5. Potentials of Pt and Au electrodes in 1 M HNO_3 at a dose strength of $3.1 \cdot 10^{15}$ ev/cm^3 · sec: 1) Pt electrode; 2) Au electrode.

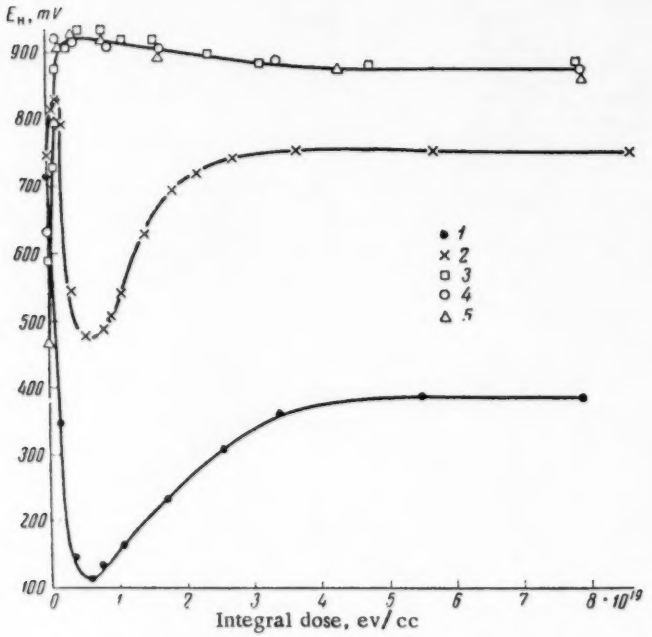

Fig. 6. Potentials of Pt and Au electrodes in irradiated $NaNO_3$ solutions: 1) 0.05 M Pt; 2) 1 M Pt; 3) 4 M Pt; 4) 0.05 M Au; 5) 4 M Au; d. s. = $2.6\text{-}3.1 \cdot 10^{16}$.

the two electrodes in 0.05 and 4 M $NaNO_3$ solution and for a Pt electrode in 1 M $NaNO_3$ solution. Stationary potentials were also established in this case, but all the curves were 200-300 mv more negative than curves in acid solutions. The potential of the Au electrode was completely independent of the solution concentration. As in acid solutions, the course of the change in the Pt electrode potential depended on the dose strength; Fig. 7 shows curves obtained at dose strengths of $2.6 \cdot 10^{16}$, $1.6 \cdot 10^{16}$, and $0.65 \cdot 10^{16}$ ev/cm^3 · sec. A fall in dose strength by a factor of 1.6 was sufficient to eliminate the minimum from the curve. After irradiation had

been stopped, the potential reached a new stationary value after a few minutes and this was almost the same in all three cases (615, 595, and 605 mv).

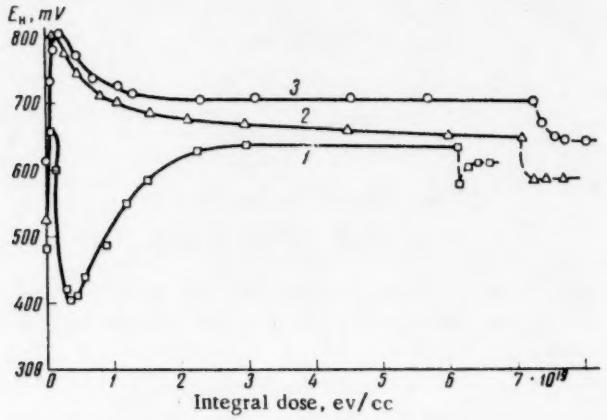

Fig. 7. Potential of Pt electrode in 1 M $NaNO_3$ at various dose strengths: 1) $2.6 \cdot 10^{16}$ ev/cm³·sec; 2) $1.6 \cdot 10^{16}$ ev/cm³·sec; 3) $0.65 \cdot 10^{16}$ ev/cm³·sec; ——— during irradiation; - - - - after irradiation had stopped.

DISCUSSION OF EXPERIMENTAL RESULTS

The reactions occurring on platinum and gold electrodes and determining their potentials in nitrate solutions depend on the nature and concentration of the products formed under the action of radiation. The observed change in potential during irradiation is associated with the competition of various electrode reactions as a result of the change in the solution composition. The fact that, during irradiation, the electrode potential differs from the value that it acquires after irradiation has been stopped shows that the electrode reactions involve short-lived intermediate or gaseous products of radiation processes, whose concentration changes when the action of radiation stops.

The stable products of radiation processes in nitrate systems are nitrate or nitrous acid, hydrogen peroxide, oxygen, and hydrogen, which are formed in yields that depend on the concentration of NO_3^- and H^+ ions and also on the dose strength [6-8]. The main reactions leading to their formation due to primary radiolysis of water may be reduced to the following:

$$H + NO_3^- \rightarrow NO_2 + OH^- \quad (1)$$

with subsequent dimerization and hydrolysis as follows:

$$2NO_2 \rightarrow N_2O_4 \quad (1a)$$

and

$$N_2O_4 + H_2O \rightarrow NO_3^- + H^+ + HNO_2; \quad (1b)$$

$$2H \rightarrow H_2; \quad (2)$$

in places of high ionization density and

$$2OH \rightarrow H_2O_2 \quad (3)$$

both in places of high ionization density and in the whole volume.

With an increase in the concentration of NO_3^- ions, there is an increase in the consumption of H atoms through reaction (1) and a corresponding increase in the number of free OH radicals. It may be assumed that in competition with reaction (3) there is the reaction

$$NO_3^- + OH \rightarrow NO_3 + OH^-. \quad (4)$$

Subsequent dimerization and hydrolysis, according to the equations

$$2NO_3 \rightarrow N_2O_6, \quad (4a)$$

$$N_2O_6 + H_2O \rightarrow HNO_4 + HNO_3, \quad (4b)$$

$$HNO_4 + H_2O \rightarrow HNO_3 + H_2O_2, \quad (4c)$$

in analogy with the scheme adopted for the formation of pernitric acid [9], should lead to the same final yield of H_2O_2 as reaction (3). Oxygen appears mainly as a secondary product as a result of catalytic or radiation decomposition of hydrogen peroxide [6]

$$H_2O_2 \rightarrow H_2O + \frac{1}{2} O_2. \quad (5)$$

With sufficiently concentrated solutions of NO_3^- ions, reaction (1) is able to compete with reaction (2) in places of high ionization density. This leads to a fall in the yield of molecular hydrogen as we showed for x-radiation [6] and Sowden showed for mixed radiation of a nuclear reactor [10]. The data obtained in the two investigations agreed well. In acid solutions there occurs a nonradiation reaction [11]

$$HNO_2 + H_2O_2 \longrightarrow HNO_3 + H_2O, \quad (6)$$

leading to a fall in the concentration of products from the radiation process. This is responsible for the fact that it was not possible to detect hydrogen peroxide in an irradiated 1 M solution of HNO_3 and the concentration of HNO_2 did not exceed $3\text{-}4 \cdot 10^{-4}$ M, while in 1 M $NaNO_3$ solution the concentrations of H_2O_2 and NO_2^- could reach approximately 10^{-2} M.

The HNO_2 concentration in solution also depends on the equilibrium relations

$$2HNO_2 \rightleftarrows H_2O + N_2O_3 \quad \text{and} \quad N_2O_3 \rightleftarrows NO + NO_2. \quad (7)$$

With the continuous passage of gas (N_2) through the solution, part of the HNO_2 formed disappears due to entrainment of NO and NO_2. In neutral and alkaline solutions, the concentration of NO_2^- ions has a definite value for each dose, but the H_2O_2 concentration may vary considerably due to catalytic decomposition reactions, which are difficult to assess. As for HNO_2, it is therefore necessary to determine the H_2O_2 in each particular case for a given dose.

Together with nitrogen oxides, the gas stream carries off the molecular hydrogen and oxygen formed in the solution, and their partial pressure over the solution depends on their radiation yield, the dose strength, and the nitrogen flow rate. As was shown by Monk and Ellingham [12] and also Vetter [13], who investigated the mechanism of the corresponding electrode process, in 1-12 M HNO_3 solution containing HNO_2 in concentrations of $3 \cdot 10^{-3}$ to $3 \cdot 10^{-1}$ M, on a platinum electrode there is established an equilibrium potential corresponding to

$$E = 0{,}94 + \frac{RT}{2F} \ln \frac{(NO_3^-)(H^+)^3}{(HNO_2)}. \quad (8)$$

In special experiments, we showed that this relation is obeyed for Pt and Au electrodes in 1 M HNO_3 and 0.5 M HNO_3 solutions if the HNO_2 concentration is no lower than approximately $2 \cdot 10^{-4}$ M and approximately 10^{-3} M, respectively. In contrast to this, the NO_3^- / NO_2^- couple, which appears during irradiation in neutral and alkaline

solutions, is unable to impose a potential on the electrode. Thus, the stable couples which are capable of determining the equilibrium potential in these systems after the end of irradiation may only be $\frac{HNO_3}{HNO_2}$ in an acid medium and $\frac{O_2}{H_2O_2}$ in a neutral medium.

Figure 8 gives curves of the change in potential of Pt and Au electrodes in 1 M HNO_3 solution during and after irradiation, the accumulation of HNO_2 in solution, and the equilibrium potential calculated for each experimentally determined HNO_2 concentration in relation to dose. The potentials of the Pt and Au electrodes, which differed by approximately 75 mv during irradiation, became the same a few minutes after the end of irradiation within the limits of reproducibility of the data (approximately 10 mv) and equalled the equilibrium potential calculated from the ratio of HNO_3 and HNO_2. This correspondence was not observed in 0.5 M HNO_3 solution as the actual HNO_2 concentration was so low ($> 10^{-4}$ M) that, as was shown above, the equilibrium potential could not be established on the electrode.

After the end of irradiation in $NaNO_3$ solutions, it might be expected that an equilibrium potential would be established on the electrode corresponding to the H_2O_2 and O_2 content in accordance with the equation

$$E_H = 0{,}682 + \frac{RT}{2F} \ln \frac{(O_2)(H^+)^2}{(H_2O_2)}. \qquad (9)$$

In actual fact, this did not occur. In 1 M $NaNO_3$ solution at pH 6.5, the potential established after the end of irradiation (approximately 600 mv, see Fig. 7) was several tenths of a volt more positive than that calculated from the H_2O_2 concentration (equal to approximately 10^{-3} M at a dose of approximately $5 \cdot 10^{19}$ ev/cm^3 [4]) and the partial oxygen pressure ($p_{O_2} = 2.6 \cdot 10^{-4}$ atm, corresponding to a yield G $(O)_2 = 0.42$ at a dose strength of $2 \cdot 10^{16}$ ev/cm^3 · sec [6]). The potential established after the end of irradiation, thus, is not determined by the $\frac{O_2}{H_2O_2}$ couple in the solution and evidently corresponds to the presence on the electrode surface of some oxides both present in the initial state and formed under the action of the radiation.

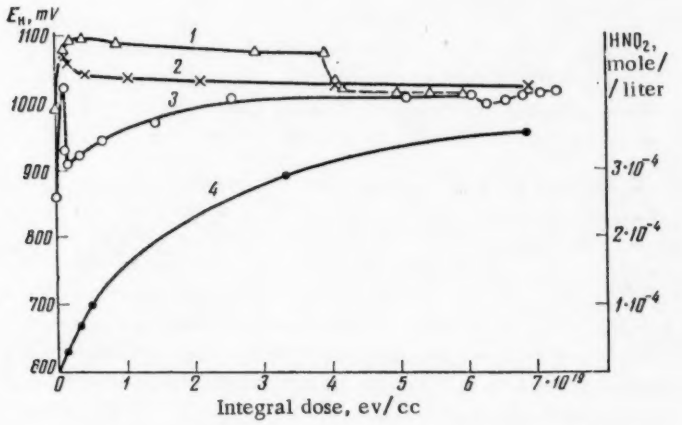

Fig. 8. Comparison of the potentials of Pt and Au electrodes in 1 M HNO_3 with the equilibrium potential $E_H = 0{,}94 + \frac{RT}{2F} \ln \frac{(NO^-_3)(H^+)^3}{(HNO_2)}$

1) Potential of Au electrode; 2) calculated equilibrium potential; 3) potential of Pt electrode; 4) concentration of HNO_2 formed; —— during irradiation; - - - - after irradiation; d. s. = $= 3.1 \cdot 10^{16}$.

The change in potential during irradiation shows the following characteristics: a sharp displacement in a positive direction at the very beginning of irradiation with the retention of high positive values with a further increase in dose in the case of a Au electrode and with a subsequent displacement in a negative direction at a definite relation of dose strength and concentration in the case of a Pt electrode. The first effect is associated with the participation of an unstable oxidant in the electrode reaction, as after the irradiation is stopped the potential is displaced in a negative direction and after a few minutes it reaches a new stationary value (see Figs. 3, 5, 7, etc.). The reaction is apparently the same on the two electrodes (see Fig. 5, curve 3, Fig. 6, etc.). The duration of the fall makes it improbable that there is direct participation of primary OH radicals in the electrode process. In the case of a Pt electrode, the displacement in a positive direction is specific for nitrate solutions, is independent of acidity, and requires a sufficiently high concentration of NO_3^- ions. This makes it possible to assume that it is caused by higher oxides of nitrogen formed from NO_3^- ions, such as NO_3 by reaction (4); the fall in potential at the end of irradiation in this case may correspond to the occurrence of reactions (4a), (4b), and (4c). In addition to the processes examined, on the Pt electrode there may evidently occur ionization of hydrogen, arising in solution under the action of the radiation. It is natural to associate with this process the above-mentioned displacement of the potential in a negative direction in irradiated nitrate solutions as it was impossible to detect in them products of deeper reduction than NO_2^- and NO and the latter could not cause such negative potentials. In nitrate solutions, in which reaction (1) proceeds with high efficiency, it is improbable that H atoms participate in the electrode process and the displacement in potential is apparently completely caused by ionization of molecular hydrogen.

An examination of curves showing the relation of Pt-electrode potential to dose indicates a definite parallelism between the stationary concentration of molecular hydrogen in the solution and the magnitude of the displacement. In actual fact, the displacement in potential falls as the NO_3^- concentration increases in 0.05, 0.5, and 1 M HNO_3 and $NaNO_3$ solutions at a dose strength of $2.6\text{-}3.7 \cdot 10^{16}$ ev/cm^3 · sec and is absent at the same dose strength in 4 M solutions, while at $0.3\text{-}1.6 \cdot 10^{16}$ ev/cm^3 · sec it is also absent in 0.5 and 1 M HNO_3 and $NaNO_3$. For calculating the partial pressure of hydrogen over the irradiated solutions, we used values of the hydrogen yield taken directly and interpolated from data we obtained [6].

Concentration NO_3^- in M/liter	0,05	0,1	0,5	1	4	5
$G(H_2)$ molecules/100 eV	0,5	0,5	0,3	0,18	0,05	0,05

The partial hydrogen pressures from $3.2 \cdot 10^{-4}$ to $1 \cdot 10^{-4}$ atm, which were established for various concentrations and dose strengths corresponded to falling values of the potential displacement, while there was no displacement in a negative direction at pressures from $6 \cdot 10^{-5}$ to $1 \cdot 10^{-5}$ atm. The stationary hydrogen concentrations in the solution equalled $3 \cdot 10^{-7}$ to $8 \cdot 10^{-8}$ M and $5 \cdot 10^{-8}$ to 10^{-9} M, respectively.

The hypothesis that the observed potential displacement in a negative direction is determined by ionization of molecular hydrogen agrees well with data presented in Fig. 9, which shows the change in potential of a Pt electrode in 0.5 M HNO_3 during irradiation by solid lines and after irradiation by a broken line. When the radiation was switched on again for 1 minute at point C on curve 1, the potential was displaced in a positive direction and then, without radiation, described the same curve with a deep minimum as with radiation if the nitrogen flow was stopped (curve 3) and a curve with a very slight minimum and an earlier return to a stationary value with the passage of gas (curve 2). From a comparison of these curves, it follows that the potential displacement in a negative direction is caused by a gaseous product formed during irradiation, which may only be molecular hydrogen in the given case. An analogous post-radiation change in the Pt-electrode potential, which may also be ascribed to molecular hydrogen, is also observed in 1 N H_2SO_4. The initial potential E_H = + 800 mv is displaced after irradiation for 30 seconds (dose $7.8 \cdot 10^{17}$ ev/cm^3) to E_H = + 300 mv, then during 90 seconds after the cessation of irradiation, to E_H = + 26 mv, and finally returns to more positive values, reaching E_H = = 680 mv after 35 minutes.

Thus, the general course of the Pt-electrode potential in irradiated nitrate solutions may be explained qualitatively by the following succession of electrode reactions. At the very beginning of irradiation, higher oxides (supposedly NO_3), which appear in solution in a yield of the order of the yield of OH radicals ($G \geq 3$), cause a potential displacement in a positive direction. The molecular hydrogen formed simultaneously at a

yield an order lower [$G(H_2) \leq 0.5$] reaches a stationary concentration after a short time and this may be insufficient (approximately 10^{-8} M) or sufficient (approximately 10^{-6} M) to displace the potential in a negative direction. In the most favorable cases, the potential approaches the hydrogen potential. The third product formed simultaneously in acid solutions is HNO_2, but the couple HNO_3/HNO_2 is only able to affect the electrode potential at a sufficiently high HNO_2 concentration. With the accumulation of HNO_2, the potential is displaced in a positive direction and reaches a stationary value at doses of $3\text{-}5 \cdot 10^{19}$ ev/cm^3. The addition potential displacement after the end of irradiation apparently corresponds to the final removal of gaseous products.

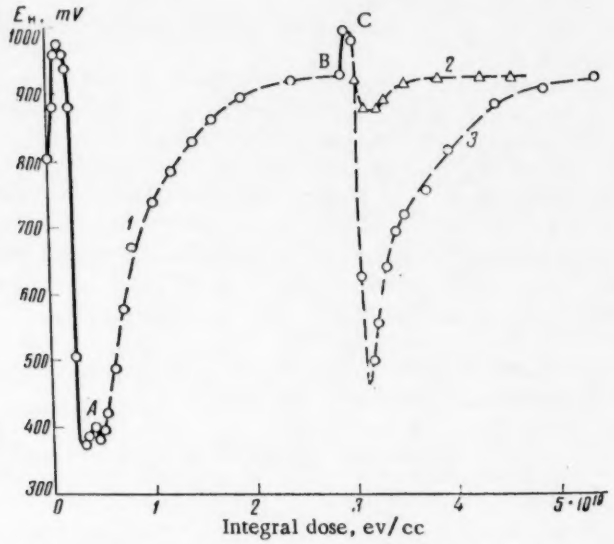

Fig. 9. Potential of Pt electrode in 0.5 M HNO_3: 1,2) with the passage of nitrogen; 3) without the passage of nitrogen; —— during irradiation; - - - - after irradiation; d. s. = $= 2.6 \cdot 10^{16}$ ev/cm^3 · sec.

It is interesting to compare the change in the Pt-electrode potential during cathode reduction of nitric acid with its change during irradiation. Beinert and Bonhoeffer [14] observed that during momentary cathode polarization in concentrated HNO_3, there is a sharp displacement of the Pt-electrode potential from $E_H = 1.26$ to 0.05 v; when the current has been switched off, the potential remains for some time close to the hydrogen potential and then suddenly returns to the initial value. These authors explained the initial predominance of the liberation of hydrogen by the very low rate of HNO_3 reduction in the absence of HNO_2 and its autocatalytic acceleration with a sharp change to the corresponding potential after some accumulation. At a lower current density, the initial displacement to the hydrogen potential is not observed. The change in potential described is very similar to that produced by brief irradiation (Fig. 8). It is evident that in both cases the displacement toward the hydrogen potential is associated with the need for the accumulation of HNO_2. In more complex solutions in which other ions, for example, cations of variable valence, participate in the oxidation and reduction reactions in addition to NO_3^- ions, the change in potential during irradiation depends on the magnitude of the exchange current at the electrode of various couples produced by the action of radiation.

SUMMARY

1. The changes in potential of platinum and gold electrodes in nitric acid and sodium nitrate solutions under the action of x-radiation were studied.

2. From the nature of the dose dependence of the potential at various concentrations and acidities of the solution and with various dose strengths it follows that the establishment of the potential involves both products from radiation conversions of nitrate ions and, in the case of a platinum electrode, a product from primary radiolysis of water, namely, molecular hydrogen.

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STERIC HINDRANCE AND THE CONFORMATION OF MOLECULES

COMMUNICATION 3. MOLECULAR AND CRYSTAL STRUCTURE OF 2,6-DICHLORO-4 NITRODIMETHYLANILINE

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The crystal structure of 2,6-dichloro-4-nitrodimethylaniline was studied for determining the bond lengths and valence angles and establishing the structure of the dimethylamino group (planar or pyramidal) and also the actual conformation of the molecule. The last problem is of particular interest as there is considerable steric hindrance in the molecule between the dimethylamino group and the chlorine atom.

Structure determination. Crystals from methanol and ethanol solutions were light yellow, highly elongated plates (long direction – a axis). The elementary forms were pinacoid {010} (main faces of the plate) and two rhombic prisms {110} and {011}. The symmetry of x-ray diffraction patterns established the Laue class as mmm of the rhombic crystal system. Determination of the periods from oxcillation x-ray patterns led to the following parameters for the elementary cell:

$a = 4{,}90 \pm 0{,}02$ Å $M = 235{,}1$
$b = 19{,}45 \pm 0{,}07$ Å $d_{meas} = 1{,}6$ g/cm³
$c = 10{,}05 \pm 0{,}05$ Å $d_{calc.} = 1{,}65$ g/cm³
$V = 958$ Å³ $n = 3{,}9$ (4)

The systematic extinctions unequivocally determined the space group as V_h^{14} = Pbcn; the molecules in a particular position lie on the axes 2. Two other particular positions with a symmetry of $\bar{1}$ were eliminated due to disagreement with the natural symmetry of the molecule.

For calculating the three-dimensional electron density series, we used a camera for photographing the reciprocal lattice to obtain developments of the layer lines 0k*l*, 1k*l*, 2k*l*, 3k*l*, hk0, and hk1 (backing of three plates; unfiltered Mo radiation). The intensities of the reflections were estimated visually from blackening marks with an accuracy of approximately 20% according to the scatter of values from different x-ray diffraction patterns. In converting the intensities into structural factors, we considered only the polarization factor and the Lorentz factor. The determination of the structure began with the calculation of the projection of the interatomic function P (0yz) on the bc face. The coordinates of the Cl atom found from it were used to determine the signs of F_{0kl}; we then calculated the electron density projection ρ(0yz), which showed all the atoms (except hydrogen). We recalculated the structural amplitudes F_{0kl}, allowing for all the atoms and using the atomic curves of Viervoll and Ogrim [1] (the same curves were used later), and found the second approximation of ρ (0yz); the number of independent terms in the series was 108. The coordinates of the atoms from this approximation (Table 1), which were determined by exponential interpolation [2], were used for calculating the third variant of ρ(0yz). The fact that all the signs were unchanged showed that the possibilities of the bc projection were exhausted; R = 0.16. Having found the y and z coordinates in this way, we calculated the x coordinates,

assuming standard bond lengths. The $\underline{x}$ coordinates were thus determined with an accuracy up to the sign; for C_2, C_3, Cl and O we adopted positive values and for $C_6(CH_3)$ it was possible to adopt only a negative value of $\underline{x}$ or otherwise the CH_3 . . . Cl distance in the molecule was improbably small (approximately 2.7 A; with $\underline{x} < 0$ we have approximately 3.2 A; the sum of the radii $Cl + CH_3 \approx 1.8 + 2.0 = 3.8$ A). Then by calculating F_{hk0} and constructing the electron density projection $\rho(xy0)$ on the ab face, we refined the values adopted

TABLE 1

Coordinates of Atoms and Heights of Maxima of Three-Dimensional Series

Atom	Two-dimensional series			Three-dimensional series			ρ in el/A^3	
	x	y	z	x	y	z	meas.	calc.
C_1	0	0,108	1/4	0	$0,107_7$	1/4	13,4	10,1
C_2	0,163	0,070	0,157	$0,168_6$	$0,071_8$	$0,163_2$	10,8	10,1
C_3	0,166	0,000	0,157	$0,167_6$	$0,001_0$	$0,160_6$	10,9	10,1
C_4	0	—0,003	1/4	0	$-0,033_0$	1/4	12,0	10,1
$C_6(CH_3)$	—0,070	0,217	0,132	$-0,076_7$	$0,218_0$	$0,130_3$	9,8	10,1
N_1	0	0,176	1/4	0	$0,180_1$	1/4	12,4	12,2
N_4	0	—0,109	1/4	0	$-0,106_7$	1/4	13,8	12,2
O	0,170	—0,131	0,183	$0,172_4$	$-0,133_2$	$0,177_3$	12,4	14,5
Cl	0,388	0,110	0,053	0,3910	0,1101	0,0524	34,6	37,2
Cl (theor.)*				0,3796	0,1155	0,0545	—	—
H(C_3)**				$0,297_3$	$-0,026_6$	$0,091_6$	—	—
Center of nucleus***				0	$0,036_7$	1/4	—	—

* Coordinates of the ideal position of the chlorine atom, which it would occupy with the valence angles C − C − Cl = 120°.

** The coordinates were calculated with the assumption that C − C − H = 120°; C − H = 1.08 A.

*** Coordinates of the center of gravity of the benzene nucleus.

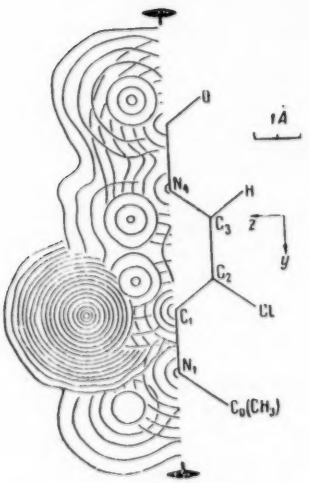


Fig. 1. Cross sections of three-dimensional electron density series parallel to bc and passing through the centers of the atoms. The contour lines are at intervals of 2 el/A^3

for $\underline{x}$. The coordinates of the atoms (Table 1) were determined by interpolation; the number of independent terms in the series was 74. Calculation of F_{hk0} from the data of this projection gave R = 0.2; no second approximation was calculated. The final refinement was made by calculating the three-dimensional electron density series $\rho(xyz)$, which is shown in Fig. 1. The signs of F_{hkl} were determined by $\underline{y}$ and $\underline{z}$ from $\rho(0yz)$ and by $\underline{x}$ from A(xy0); at this stage R = 0.16.

In the calculation of the series, the $\underline{x}$ axis was divided into 48 parts, the $\underline{y}$ axis into 120, and the $\underline{z}$ axis into 60; the number of independent terms in the series was 679. The coordinates of the atoms, which were obtained from this series by exponential interpolation (Table 1), changed somewhat in comparison with the given projections. Calculation of F_{hkl} from the results of ρ (xyz) gave R = 0.12 and comparison of F_{meas} with F_{calc} led to a thermal factor with B = 3.7 A^2. The second approximation of ρ (xyz) was not calculated. According to the formulas of Vainshtein [3], when B = 3.7 A^2 and $s_{break} = \sin\vartheta/\lambda \approx 1.0$,* we obtain for the error in the interatomic distances ± 0.01 A and the error in the electron density ± 0.3 el/A^3. This error corresponds to an error in the determination of the valence angles of ± 2°. Table 1 gives the heights of the maxima found and calculated according to Vainshtein; the agreement is good in general and the nature of the discrepancies between ρ_{meas} and ρ_{calc} shows the important role of torsional vibrations of the molecule about axis 2 in the general picture of thermal motion.

Molecular structure. The 2,6-dichloro-4-nitrodimethylaniline molecule is a good example of the establishment of a real conformation

* $1/\lambda_{Mo} = 1.4$ A^{-1}, but even at $\vartheta > 45°$, as a rule, the intensities were too small to measure and therefore s_{break} was taken as equal to sin 45°/0.71 = 1.0 A^{-1}.

as a result of the interaction of several factors: steric hindrance, flexibility of the valence angle, and the tendency to coplanarity. The geometric parameters of the molecules, calculated from the coordinates from the three-dimensional electron density series, are given in Fig. 2. The differences in the bond lengths in the benzene nucleus correspond to the experimental error; the mean $C-C = 1.38_4$ A is close to the standard value 1.395 A [4]. The bond length $C-Cl = 1.72_7$ A agrees with that found in o-dichlorobenzene (1.73_8 A [5]), but is somewhat greater than the standard value of 1.70 A [4].

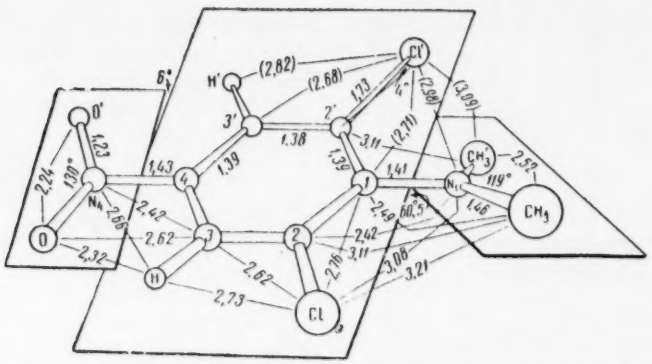


Fig. 2. Structure of 2,6-dichloro-4-nitrodimethylaniline molecule. The C−Cl bonds deviate from the ideal directions by 4°. The distances for the ideal directions of these bonds are given in brackets.

The molecule in the crystal lies on the axis of symmetry 2, which passes through the atoms N_1, C_1, C_4, and N_4 (Figs. 1 and 2). Therefore, the benzene nucleus, the nitro group, and the dimethylamino group are found to be planar. The equations of the planes have the form (coordinates in A):

Benzene nucleus	$0.732\,x + 0.681\,y - 1.711 = 0$
Nitro group	$0.654\,x + 0.757\,y - 1.902 = 0$
Dimethylamino group	$0.954\,x + 0.300\,y - 0.754 = 0$

At the same time, the molecule as a whole is nonplanar; the nitro group and dimethylamino group are displaced from the plane of the nucleus by rotation about the N−C bonds in opposite directions (Fig. 2):

$$\varphi_{NO_2} = 6°;\ \varphi_{N(CH_3)_2} = -60{,}5°.$$

In molecules of the type examined, in the absence of steric hindrance one would expect a coplanar conformation and the greatest shortening of the $C_{ar}-N$ bond lengths in comparison with the standard value for a single bond of 1.472 A [4] as conjugation should appear most clearly:

In actual fact, in the coplanar molecule of p-nitroaniline [6], $C-N\ (O_2) = 1.41$ A and $C-N\ (H_2) = 1.37$ A.

Substituents in the position ortho to the nitro or dimethylamino group create considerable steric hindrance, which may lead to disruption of the coplanarity of these groups with the benzene nucleus. Such rotation about the C−N bonds must hinder conjugation as the conjugation energy equals $\sim \cos^2 \varphi$, where φ is the angle between the planar parts of the molecule connected formally by a single bond, through which conjugation is transmitted [7]. At small rotations, the conjugation energy changes inappreciably (at $\varphi = 10°$, only by 3%) so that slight disruption of coplanarity may be observed as a result of the effect of the strong field of the crystal.

In order to elucidate the characteristics of the actual conformation, it is necessary to compare the measured distances between atoms that are not bound by valences (Fig. 2) with the corresponding distances in the ideal coplanar conformation (Fig. 3). This hypothetic model was constructed with the ideal valence angles of 120° and the standard bond lengths [4] apart from the $C_1 - N_1$ and $C_4 - N_4$ bonds for which we took the values found in p-nitroaniline (coplanarity). Unfortunately, the analysis of steric hindrance does not give definite information on the orientation of the CH_3 groups in the dimethylamino group. The sum of the shortened distances between the hydrogen atoms of the CH_3 groups and the other neighboring atoms hardly changes with rotation of these groups about the $N_1 - C_0$ bonds (both in the actual and in the coplanar conformations). Therefore, it is possible to assume "free rotation" (statistical disorder) of the methyl groups and regard them as spheres of radius $R_{CH_3} = 2.0$ A (mean of the dimensions of the CH_3 group in different directions).

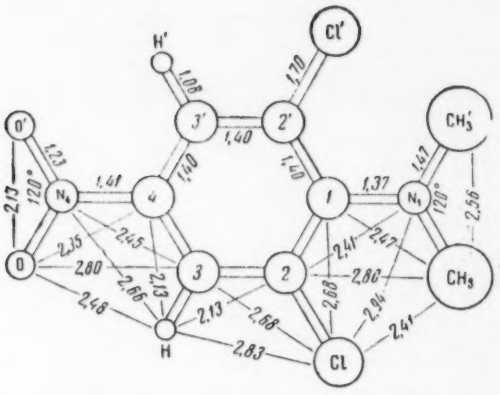


Fig. 3. Ideal coplanar conformation of the molecule.

Although the molecule does not have substituents in the positions ortho to the nitro group, slight steric hindrance between the atoms of this group and the ortho carbon and hydrogen atoms of the nucleus still exists (Fig. 3): O . . . H = 2.48 A instead of the sum of the intermolecular radii $R_O + R_C = 1{,}38 + 1{,}17 = 2{,}25$ Å ($\Delta = 0{,}07$ Å); O... C = 2,80 Å instead of $R_O + R_C = 1{,}38 + 1{,}77 = 3{,}15$ Å ($\Delta = 0{,}35$ Å). Such slight shortenings are readily overcome by the tendency to coplanarity (p-nitroaniline, for example). Therefore, the rotation of the nitro group by $\varphi = 6°$ should be ascribed to the effect of the force field of the crystal. In actual fact, in the crystal of p-dinitrobenzene (with the same steric hindrance at the nitro group as in the given case and in the p-nitroaniline molecule), the nitro groups are also displaced from the plane of the nucleus by $\varphi = 9.5°$ [8].

The bond length $C_4 - N_4 = 1.43$ A is somewhat greater than in p-nitroaniline (1.41 A), but appreciably less than in p-dinitrobenzene (1.48 A). Such a relation is quite logical as conjugation is expressed more strongly in p-nitroaniline and is practically absent in p-dinitrobenzene. The bond length $N_4 - O = 1.23$ A is also intermediate: in p-nitroaniline it is 1.27 and in p-dinitrobenzene, 1.21 A. The distance O . . . O' = 2.13 A in the nitro group with the ideal angle O − N − O = 120° and N − O = 1.23 A would be shortened by 0.63 A ($2R_O = 2.76$ A). In the actual molecule this shortening is reduced to 0.52 A (O . . . O' = 2.24 A) due to an increase in the valence angle to 130°. In the other cases investigated, the increase in angle was less: in p-dinitrobenzene and p-nitroaniline, the angle was 124°. The additional increase in the structure examined may be explained by packing characteristics.

No less substantial steric hindrance exists in the dimethylamino group. An appreciable increase in the C − N − C valence angles in comparison with the theoretical value of 90° was therefore to be expected. We should point out that even in the ammonia molecule, the valence angle is 107° ± 4° [9]. In addition, in the structures

there should be a tendency for the nitrogen atom to adopt a planar configuration, which is observed, in particular, in urea whose molecule (including the hydrogen atoms) was found to be planar with a nitrogen valence angle of 119 ± 2° [10]. In our case, both these factors act in the same direction and the dimethylamino group is found to be planar with a valence angle $C_0 — N_1 — C_0' = 119°$. The bond length $N_1 — C_0(CH_3) = 1{,}46$ Å practically coincides with the standard length of a single bond C—N = 1,47 Å. On the other hand, the bond length $C_1 — N_1 = 1{,}41$ Å is substantially shortened, which indicates conjugation of the dimethylamino group with the nucleus. However, due to rotation of the dimethylamino group by 60.5°, this conjugation is found to

be less complete than in the coplanar p-nitroaniline molecule, where $C_1—N_1(NH_2) = 1{,}37$ Å, i.e., the shortening is appreciably greater.

The hypothetical coplanar conformation of the 2,6-dichloro-4-nitrodimethylaniline molecule is characterized by very great steric hindrance (Fig. 3 and Table 2). An example of an inadmissibly small distance is $CH_3 \ldots Cl = 2.41$ A instead of $R_{CH} + R_{Cl} = 2{,}0 + 1{,}8 = 3{,}8$ Å; $\Delta = 1{,}4$ Å. This hindrance may be decreased by rotation of the dimethylamino group about the $C_1 - N_1$ bond and deviation of the C—Cl bonds from the ideal direction (withdrawal of the chlorine atoms from the dimethylamino group). Distortion of the C_1 and N_1 valence angles, which has little effect on the distances between atoms that are not bound by valences, is less probable. In actual fact, the true conformation of the molecule (Fig. 2) differs from the ideal as a result of both of these deformations: rotation of the dimethylamino group by 60.5° and distortion of the C—C—Cl valence angles by 4° (the $C_1—C_2—Cl$ angle is increased to 124° so that the chlorine atom is displaced from the ideal position by 0.12 A; the angle between the C—Cl bond and the plane of the nucleus is 1.5°). The steric hindrance in the actual conformation is appreciably decreased: the sum of the shortenings is 7.08 A instead of 9.44 A in the ideal conformation(Table 2). Had the C—Cl valence had an ideal direction, the hindrance would have been somewhat greater (figures in brackets in Table 2 and Fig. 2): the sum of the shortenings would have been 7.32 A instead of 7.08 A in the actual conformation. The steric hindrance would be minimal with the dimethylamino group perpendicular to the benzene nucleus (rotation angle $\varphi = 90°$). Table 2 also gives data for this conformation which is "optimal" with respect to steric hindrance (experimental bond lengths and valence angles were used apart from $C—C—Cl = 120°$ and $C_1—N_1 = 1{,}47$ Å · in the absence of conjugation). However, at $\varphi = 90°$, conjugation of the dimethyl-

TABLE 2

Distances Between Atoms That Are Not Bound By Valences in the 2,6-Dichloro-4-Nitrodimethylaniline Molecule in Relation to the Rotation of the Dimethylamino Group and the C—C—Cl Valence Angles.

d is the distance in A; ΣR is the sum of the intermolecular radii in A ; $\Delta = \Sigma R - d$ is the shortening in A; $\Sigma\Delta$ is the sum of the shortenings in A; the figures in brackets refer to the case with ideal valence angles

Atoms	ΣR	Coplanar conformation $\varphi = 0°$		Actual conformation $\varphi = 60.5°$				"Optimal" conformation $\varphi = 90°$	
		d	Δ	d	Δ	d	Δ	d	Δ
$CH_3 \ldots C_2$	3,77	(2,80)	(0,97×2)	3,11	0,66×2	(3,11)	(0,66×2)	(3,37)	(0,40×4)
$CH_3 \ldots Cl$	3,80	(2,41)	(1,39×2)	3,21	0,59×2	(3,09)	(0,71×2)	(3,59)	(0,21×4)
$Cl \ldots N_1$	3,37	(2,94)	(0,43×2)	3,08	0,29×2	(2,98)	(0,39×2)	(2,98)	(0,39×2)
$Cl \ldots C_1$	3,57	(2,68)	(0,89×2)	2,76	0,81×2	(2,71)	(0,86×2)	(2,71)	(0,86×2)
$Cl \ldots C_3$	3,57	(2,68)	(0,89×2)	2,62	0,95×2	(2,68)	(0,89×2)	(2,68)	(0,89×2)
$Cl \ldots H$	2,97	(2,83)	(0,15×2)	2,73	0,24×2	(2,82)	(0,15×2)	(2,82)	(0,15×2)
$\Sigma\Delta$			(9,44)		7,08		(7,32)		(7,02)

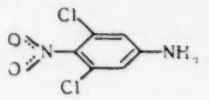
amino group with the nucleus would be impossible and this is energetically unfavorable. Therefore, in actual fact there is a compromise between the tendency to coplanarity ($\varphi = 0°$) and the retention of undistorted angles, on the one hand, and the tendency to the minimum steric hindrance ($\varphi = 90°$), on the other. In addition, according to Table 2 a change in φ from 90° to 60° increase the hindrance only slightly. Deformation of the C—C—Cl angles also changes the steric hindrance little and therefore is found to be slight.

An analogous compromise also occurs with ortho-substituted derivatives of biphenyl [11] and many other sterically hindered conjugated systems. It is interesting that for 2,2'-dihalobiphenyls $\varphi < 90°$ (for the coplanar cis conformation $\varphi = 0°$); consequently, all these molecules have a pseudocis conformation, i.e., a twisted conformation, intermediate between the coplanar cis conformation and the "optimal" conformation with respect to steric hindrance with the nuclei perpendicular to each other ($\varphi = 90°$). Analysis of steric hindrance shows that the twisted conformations pseudocis ($0° < \varphi < 90°$) and pseudotrans ($\varphi' = 180° - \varphi$) are equivalent.

The realization of a pseudocis conformation in all these cases requires allowance not only for the repulsion but also the attraction between atoms which are not bound by valences.

The steric hindrance in the coplanar conformation is so great that rotation of the dimethylamino group must involve overcoming a substantial potential barrier. This is well illustrated by a molecular model (Fig. 4). In actual fact, analogous compounds with approximately the same steric hindrance, but with unsymmetrical substitution, can be separated into optical antipodes [11].

It is very interesting to compare the structure we studied with the structure of 3,5-dichloro-4-nitroaniline [12]:



In the crystal, this molecule is also on the axis of symmetry 2 so that the nitro group, amino group, and benzene nucleus are planar. The steric hindrance is concentrated at the nitro group and leads to results analogous to our case. The nitro group is turned through an angle $\varphi = 64°$ and the $C_4 - C_3 - Cl$ angle is increased to 123°. Conjugation of the amino group with the benzene nucleus shortens the $C_1 - N_1$ bond to 1.37 A as with p-nitroaniline. On the other hand, the bond $C_4 - N_4$ = = 1.44 A is shortened less as the conjugation of the nitro group is disrupted. The bond length C − Cl = = 1.74 A is somewhat increased, as in our structure. The sum of the shortenings in the ideal coplanar conformation is 6.74 A, i.e., somewhat less than for 2,6-dichloro-4-nitrodimethylaniline, but the angle of rotation of the nitro group is found to be greater than that of the dimethylamino group. This shows the approximate nature of characterizing steric hindrance by the sum of the shortenings.

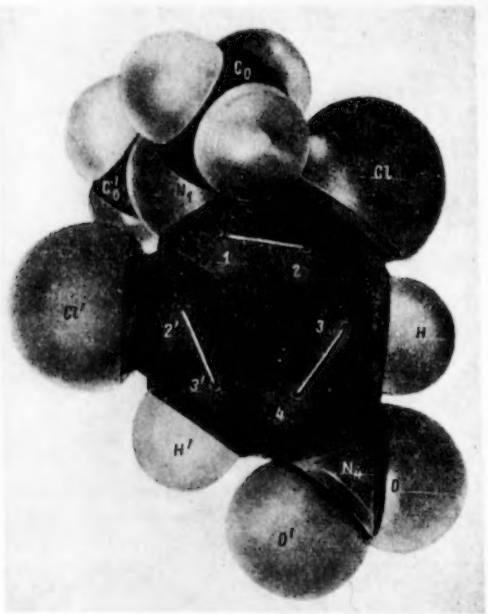


Fig. 4. Molecular model illustrating steric hindrance. The angle of rotation of the dimethylamino group is 60°.

Packing of molecules. The packing of the molecules in the crystal is shown in Figs. 5 and 6. This also shows the hydrogen atoms of the CH_3 group in the position where the Cl atom is exactly in the middle between two H atoms of the neighboring CH_3 group of the same molecule (C—H = 1,08 Å; H—C—H = 109°28′): H_1—0,49; 0,92; 4,77; H_2—1,15, 1,55, 4,96, H_3—0,75, 0,56, 3,54 (in A).

The numeration of the molecules and their symmetrical bond are as follows: I (x, y, z) starting molecule; II $(x+1/2, y+1/2, z+1/2)$ — $- n(xy1/4)$; III $(x+1/2, y+1/2, z) - 2_1[x1/40]$; IV $(\bar{x}, \bar{y}, \bar{z}) - \bar{1}\ (000)$; V $(x \pm 1, y, z)$ — translation a.

The space group Pbcn is one of the most probable ones for molecules with the crystal symmetry 2 [13] and guarantees the densest packing of them. In actual fact, the molecular coordination number equals 12. A given molecule is surrounded by and has contacts with 2 molecules of type II, 4 of type III, 4 of type IV, and 2 of type V. The true volume of the molecules, found from increment tables [13] is 176 A^3; the packing factor k = 0.73.

The shortest intermolecular distances (Table 3) give the following intermolecular radii, which agree well with tabular data: C 1,83±0,005 Å, Cl 1,82±0,005 Å, O ~ 1,36 Å. The angle between the benzene nucleus and the plane bc, $\omega = 43°$, and the distance between planes of the nucleus connected by translation a

equals 3.58 A. The superposition of the nuclei thereupon is closest packed (C . . . C contact). There is

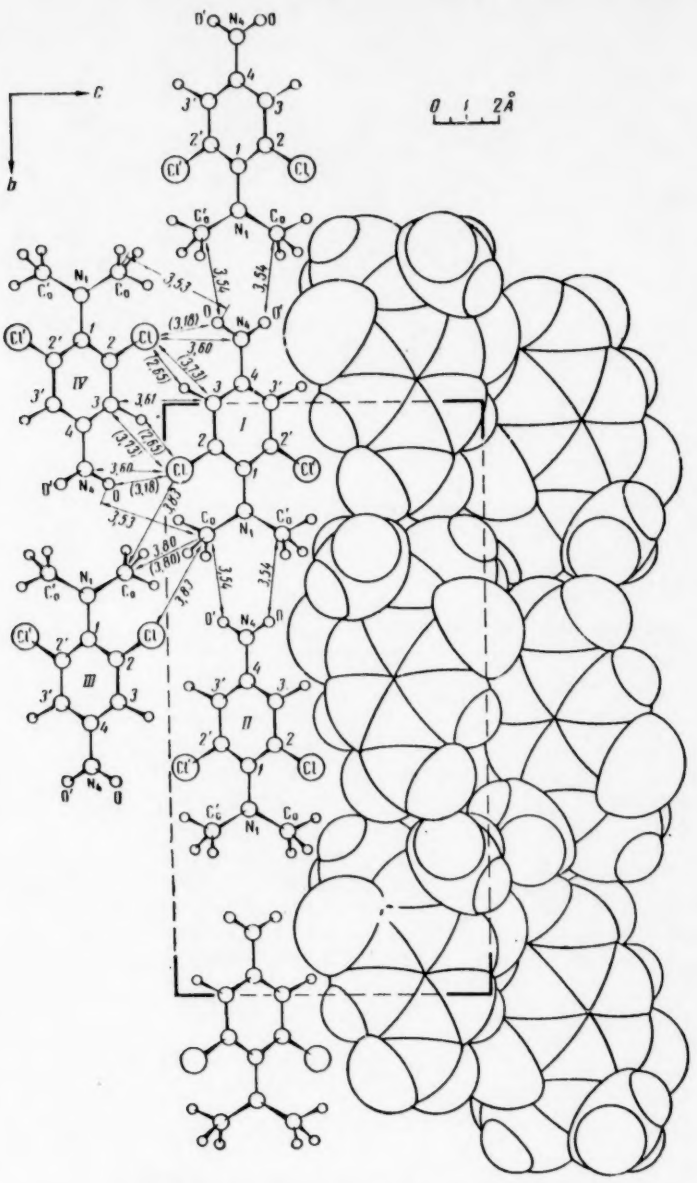


Fig. 5. Projection of structure on bc face. The figures in brackets give the distances between atoms of molecules, connected with the compulsory participation of translation a.

substantial shortening of the distance H(I)—Cl(IV) = 2,65 Å. It is possible that this shortening is caused by the tendency toward dense packing. To increase the H . . . Cl distance, it is necessary to decrease the angle of the nucleus with the plane bc and this leads to the disappearance of contact between nuclei I and V, connected by translation a. On the other hand, it is possible that the shortening of the H . . . Cl distance is fictitious due to the inaccuracy of the localization of the H atom. In actual fact, the H atom lies between the

nitro group and the Cl atom; this steric hindrance may push the H atom out of the plane of the nucleus, distorting the C – C – H angle. Appreciable disruption of additivity in the contacts involving methyl groups is not surprising due to the indefiniteness of radius of the CH_3 group.

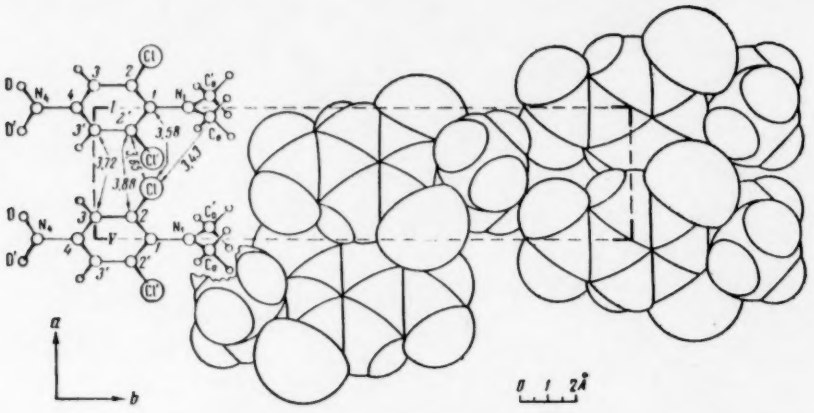


Fig. 6. Projection of structure on ab face.

TABLE 3

Shortest Intermolecular Distances (in A)*

Atoms	Distance	Sum of radii
C_3(I) . . . C_3(IV)	3,61	1,83×2=3,68
C_2(I) . . . C_2'(V)	(3,68)	1,83×2=3,68
C_3(I) . . . C_3'(V)	(3,72)	1,83×2=3,68
C_3(I) . . . Cl(V)	(3,58)	1,83+1,82=3,65
C_2(I) . . . Cl'(V)	(3,65)	1,83+1,82=3,65
C_3(I) . . . Cl(IV')	(3,73)	1,83+1,82=3,65
O(I) . . . Cl(IV')	(3,18)	1,36+1,82=3,18
CH_3(I) . . . O(IV)	3,53	2,0+1,36=3,36
CH_3(I) . . . O'(II)	3,54	2,0+1,36=3,36
CH_3(I) . . . Cl(V)	(3,43)	2,0+1,82=3,82
CH_3(I) . . . Cl(III)	3,83	2,0+1,82=3,82
CH_3(I) . . . CH_3(III)	3,80	2,0×2=4,0
N_4(I) . . . Cl(IV)	3,60	1,57+1,82=3,39
H(I) . . . Cl(IV')	(2,65)	1,17+1,82=2,99

* The figures in brackets are the distances between atoms of molecules connected with the compulsory participation of translation a.

In conclusion, the authors would like to thank A. I. Kitaigorodskii for interest in the work and P. P. Shorygin for providing the preparation for the investigation.

SUMMARY

1. The crystal structure of 2,6-dichloro-4-nitrodimethylaniline was determined; the interatomic distances and valence angles were found with accuracies of ± 0.01 A and ± 2°, respectively.

2. Steric hindrance at $CH_3 \ldots Cl$ leads to rotation of the dimethylamino group by 60.5° relative to the benzene nucleus and deformation of the C−C−Cl valence angles by 4°.

3. The loss in coplanarity disrupts conjugation in the molecule, which is reflected in the lengths of the carbon − nitrogen bonds: $C—NO_2 = 1{,}43$ Å; $C—N(CH_3)_2 = 1{,}41$ Å; $N—CH_3 = 1{,}46$ Å.

4. The actual conformation of the molecule is established as a result of a compromise between the tendencies to coplanarity, retention of normal valence angles, and minimum steric hindrance.

5. The structure is characterized by a high coordination number and density. Most intermolecular contacts occur at normal distances.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

COVALENT RADII OF CARBON AND THE CONJUGATION PROBLEM

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1. Bond length is one of the most important parameters in the structure of a molecule. The distance between any two atoms linked by a covalent bond of a definite type varies with the identities of the other atoms and groups present in the molecule, but for most elements the departure from the mean value is relatively small. As a result of this, elements can be assigned definite covalent radii, and an interatomic distance can be regarded as the sum of the two radii of the two atoms concerned in the formation of a single covalent bond. However, this relative constancy of interatomic distance is not observed in all cases. When a single carbon-carbon bond is adjacent to a double or triple bond, or to an aromatic ring, there is a considerable shortening of the bond, as compared with the interatomic distance in paraffin hydrocarbons.

The resonance-mesomerism theory explains the shortening of bonds of this type by the superposition of resonance structures; according to this theory the shortening of single C–C bonds is accompanied by the lengthening of the multiple bonds.

As will be seen from the further discussion, the true physically based cause of the shortening of single carbon-carbon bonds in unsaturated hydrocarbons lies in the reduction in the covalent radii of carbon atoms on change in the hybridization of the orbitals with transition of carbon atoms from the sp^3 state to the sp^2 or sp state.

The question of the effect of the hybridization of orbitals on the shortening of bonds was first considered by Pauling, Springall, and Palmer [1] for the case of propyne. From the fact that the C–H distance in acetylene is 1.06 A, only 0.03 A less than that in methane, but the single carbon-carbon bond in propyne is shorter than the normal C – C bond by 0.08 A (1.54 – 1.46 A), the authors concluded that not more than one-third of the shortening can be explained by the "orbital effect." In their opinion, the main cause of the shortening of the single bond in propyne is the resonance of structures of Type I (hyperconjugation):

$$\overset{+}{\mathrm{H}}\mathrm{CH_2}=\mathrm{C}=\overline{\mathrm{C}}\mathrm{H} \qquad (I)$$

The authors explain similarly the shortening of single bonds in other compounds containing double bonds: butadiyne, butadiene, aromatic hydrocarbons, etc. As is well known, this point of view has received wide acceptance.

Later, Mamotenko, Coulson, and Tatevskii turned their attention on the effect of the hybridization of orbitals of carbon atoms on the properties of organic molecules. In a paper on the calculation of bond energies and repulsions in complex systems of atoms, Mamotenko [2] showed that, contrary to Pauling's ideas, sp^2 hybridization gives a stronger, and therefore shorter bond than sp^3 hybridization. In this connection, the author points out that for the explanation of the reduced reactivity of atoms and groups attached to a double-bonded

carbon (e.g., chlorine in vinyl chloride or chlorobenzene) there is no need to bring in, as Pauling does [3], resonance structures of the type (II) and (III)

(II) (III)

Coulson [4] determined the coavlent radii of carbon and the part that they play in the shortening of bonds in the following manner. He started from the assumption that the covalent radius of hydrogen in bonds of various types is constant, namely 0.322 A. The author obtained this value of the radius of hydrogen by subtraction of the covalent radius of carbon in the sp^3 state (0.71 A) from the interatomic distance between carbon and hydrogen in methane (1.093 A). With the aid of experimental data on the C – H bond lengths in ethylene (1.071 A) and acetylene (1.057 A), Coulson concluded that the covalent radius of carbon in the sp^2 state is 0.749 A, and its radius in the sp state is 0.735 A. It follows from these magnitudes of covalent radii that in propyne, for example, the shortening of the single bond as a result of the "orbital effect" is 0.036 A, while the remaining shortening (0.046 A) is due to the delocalization of the π-electrons of the triple bond, i.e., hyperconjugation (resonance of structures of Type I).

The concept of the valence states of carbon atoms and their effect on the nature of the carbon-carbon bond is used by Tatevskii [5] in his papers on types of chemical bonds. However, he supposes that the question of whether there is a certain proportion of the π-bond between the central carbon atoms in butadiene and other similar systems cannot be resolved on the basis of bond-length measurements [6].

2. As stated above, Coulson [4] in the estimation of the covalent radii of carbon assumed that the hydrogen atom preserves a constant covalent radius in bonds of various types. However, this assumption is in no way justified. On the contrary, the covalent radius of hydrogen is very variable: depending on the nature of the atom to which hydrogen is linked, this radius varies over a wide range. Thus, in the hydrogen molecule the radius is 0.37 A, and in hydrogen fluoride it falls to 0.21 A. It may therefore be assumed that the covalent radius of hydrogen, even in hydrocarbons of various types, is not constant, but varies with the character of the hybridization of the orbitals of the carbon atom to which it is linked. In other words, the C–H bond lengths in ethylene and acetylene cannot serve as a criterion of the lengths of the covalent radii of carbon in the sp^2 and sp states.

Considerably less variation in atomic radius is observed for carbon in the sp^3 state in compounds with different elements. There is good reason, therefore, to assume the relative constancy of the radii of carbon in the sp^2 and sp states and to proceed to the determination of their values on the basis of the distances between carbon atoms in bonds of various types. With this object, it is desirable to examine the lengths of C–C bonds in molecules having bonds of an "intermediate character" and determine the extent to which the variation in the lengths of single bonds is in accord with changes in the lengths of multiple carbon-carbon bonds. As a result of conjugation (delocalization of the π-electrons of multiple bonds), the shortening of a single bond in, for example, butadiene should be accompanied by the lengthening of the double bonds, just as the lengthening of the single bond of propyne due to hyperconjugation should lead to a definite shortening of the triple bond.

An idea of the mutual changes in bond lengths which should occur in unsaturated hydrocarbons as a result of conjugation or hyperconjugation may be obtained with the aid of Pauling's curve [7] (Fig. 1), which expresses the experimental relation between bond length and bond order. In Fig. 1, bond order is plotted as abscissa, and along the axis of ordinates are plotted the lengths of carbon-carbon bonds in ethane (1.54 A, bond order 1), ethylene [8] (1.337 A, bond order 2), acetylene [9] (1.207 A, bond order 3), and two molecules with bonds of intermediate order, namely benzene [10] (1.397 A, bond order 1.5) and graphite (1.42 A, bond order $^4/_3$). The bond order is equal to one-half of the number of all the bonding electrons and depends in a definite way on the number of π-electrons in the given bond. Along the axis of abscissae is indicated the number of π-electrons localized in a bond of given order and corresponding to a definite bond length. Comparison of the departures of the lengths of single and double bonds in the molecule of any unsaturated hydrocarbon from the standard bond lengths enables one to determine whether there is delocalization of π-electrons in the given molecule and whether it affects the changes in interatomic distances.

Up to a certain time the use of Pauling's curve for this purpose was limited by the inadequate accuracy of methods for the determination of interatomic distances. With errors in x-ray and electron diffraction methods of 0.02-0.03 A it was not found possible to follow, for example, changes in the lengths of the double bond in butadiene or of the triple bond in propyne, which should occur in accordance with resonance-mesomerism theory, because these changes (0.008 A for butadiene and 0.026 A for propyne) lay within the limits of experimental error.

With the development of radiospectroscopy, which permits the determination of interatomic distances with considerably greater accuracy than x-ray and electron diffraction methods, small changes in bond length are found to be quite detectable. With the aid of radiospectroscopy many sufficiently reliable and accurately measured interatomic distances have been determined in organic molecules, and on the basis of these, it has been possible to make an experimental check on the resonance-mesomerism theory and reveal the important role for theoretical organic chemistry of the hybridization of carbon orbitals in the shortening of interatomic distances.

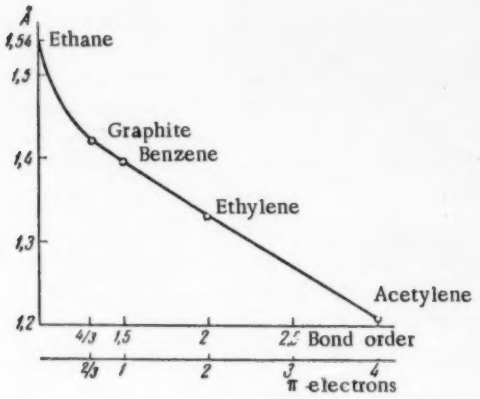
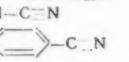


Fig. 1.

We shall begin our discussion of this question with an examination of propyne, whose interatomic distances have been determined spectroscopically within ± 0.002 A [11] (see Table 1). By the use of Pauling's curve we may determine how the length of the triple bond in propyne should change if a shortening of a single C − C bond to 1.46 A results from first-order hyperconjugation. In this case, the electron density of a single bond should increase by 0.38 π-electrons, and the electron density of a triple bond should diminish correspondingly by the same amount, which should mean a lengthening of the triple bond to 1.23 A. However, experiment shows that in propyne the triple bond has the same length as in acetylene.

TABLE 1

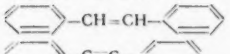
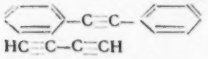
No.	Molecule	Bond lengths (A)		Literature ref.
		Single bonds	Multiple bonds	
1	Benzene		C—C 1,397₃±0,001	[10]
2	$H_2C=CH_2$		C=C 1,337	[9]
3	HC≡CH		C≡C 1,207	[8]
4	$H_2C-C\equiv CH$	C—C 1,460±0,002	C≡C 1,207±0,002	[11]
5	$H_2C-C\equiv CCl$	C—C 1,4584	C≡C 1,2069	[12]
6	$H_3C-C\equiv N$	C—C 1,460	C≡N 1,158	[13]
7	$F_3C-C\equiv N$	C—C 1,464	C≡N 1,158	[14]
8	$H-C\equiv C-C\equiv N$	C—C 1,382	C≡C 1,203; C≡N 1,157	[18]
9	$H-C\equiv N$		C≡N 1,157	[15]
10		C—C 1,419	C=C 1,402; C≡N 1,158	[19]

It follows that no delocalization of the π-electrons of the triple bond occurs, i.e., in propyne the phenomenon of first-order hyperconjugation (σ, π-conjugation) does not exist. It is evident that the observed shortening of the single C − C bond in propyne is due only to one of the two theoretically possible factors considered by Pauling, namely only to the "orbital effect," i.e., the reduction in the covalent radius of carbon in the transition from the state of tetrahedral hybridization to the state of linear hybridization. In other words, the length of the single C − C bond in propyne should be the sum of the covalent radii of carbon in the sp^3 and sp states. By subtraction of the covalent radius of carbon is a state of tetrahedral hybridization (0.77 A) from the length of the single C − C bond of propyne (1.46 A) we find the covalent radius of carbon in a state of linear hybridization (sp); it is found to be 0.69 A.

In 1-chloropropyne [12] (Table 1) the triple bond again keeps the dimensions of the triple bond of acetylene, whereas the single C – C bond is shortened to almost the same extent as in propyne. Hence, it follows from radiospectroscopic data that in propyne the covalent radius of carbon in the sp state is very close to 0.69 A. A similar picture is observed in compounds containing a triple carbon-nitrogen bond. Thus, in acetonitrile [13] and trifluoroacetonitrile [14] (see Table 1) the triple carbon-nitrogen bond has the same length as in hydrocyanic acid [15], whereas the single C – C bond length is 1.46 A in the first and 1.464 A in the second. As in propyne, in these molecules the C – C bond is of anomalous length. However, the shortening of the bonds cannot be explained by hyperconjugation because in these compounds the triple bond remained unchanged (as compared with HCN). The shortening of the bonds is to be explained by the fact that the covalent radius of carbon in the sp state is 0.69 A.

As a criterion of hyperconjugation in propyne (Baker-Nathan effect), Batuev [16] chose the C – H bond lengths of the methyl group. On the basis of an examination of the vibration frequencies of the molecules the author concluded that the bond lengths in the methyl group do not increase, so that hyperconjugation does not occur in propyne. On the basis of an examination of bond lengths in malononitrile Muller and Pritchard [17] concluded that the hyperconjugation effect is absent in this compound. The authors conclude that the shortening of single bonds in malononitrile is associated mainly with change of the covalent radii of carbon.

TABLE 2

Compound	Sum of covalent radii of carbon (A)				Lengths of multiple bond (A)			Literature ref.
	–C–C– 1,46	=C–C= 1,46	–C–C≡ 1,42	≡C–C≡ 1,38	$H_2C=CH_2$ 1,337	HC≡CH 1,207	HC≡N 1,158	
	Experimental data							
$CH_2{=}CH{-}C{\equiv}CH_2$	—	1,48	—	—	1,337	—	—	[22]
	—	1,45	—	—	1,33	—	—	[24]
	—	—	1,40	—	—	1,19	—	[25]
$HC{\equiv}C{-}C{\equiv}CH$	—	—	—	1,36	—	1,19	—	[1]
$H_3C{-}C{\equiv}C{-}C{\equiv}CH$	1,459	—	—	1,366	—	1,212	—	[26]
$H_3C{-}C{\equiv}C{-}C{\equiv}C{-}CH_3$	1,47	—	—	1,38	—	1,20	—	[1]
$H_3C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CH_3$	1,46	—	—	1,38	—	1,195	—	[27]
$N{\equiv}C{-}C{\equiv}N$	—	—	—	1,37	—	—	1,16	[1]

Data on bond lengths in propiolonitrile [18] enable us to consider the question of the structure of molecules with alternating multiple bonds. In this compound (see Table 1) the length of the triple carbon-carbon bond is somewhat less than in acetylene; the triple carbon-nitrogen bond has the same length as in hydrocyanic acid; and the single carbon-carbon bond length is 1.382 A, i.e., almost equal to double the covalent radius of carbon in the sp state. If the shortening of the single bond were due to conjugation, then (according to Pauling's curve, Fig. 1) this should lead to a total reduction in the π-electron charge in the multiple bonds by 1.2 electrons, which would lead to a lengthening of the C–C bond to about 1.246 A and of the $C \equiv N$ bond to 0.19 A.

Hence, experimental data show that leveling out of bond lengths, which would be expected if there was partial localization of π-electrons in the central C – C bond, does not occur at all in the molecule under examination. This example shows the invalidity of the mesomerism-resonance theory, according to which in systems having alternating multiple bonds there acts a mesomeric (conjugation) effect (static effect of π,π-conjugation) which causes a shortening of single bonds and a corresponding lengthening of multiple bonds. Actually, as can be seen from an examination of propiolonitrile, in a molecule containing alternating multiple bonds there occurs only the shortening of the single bond, which, as in the case of propyne, is caused by reduction of the covalent radius of carbon in the sp state to 0.69 A.

To determine the covalent radius of carbon in a state of trigonal hybridization (sp^2) an examination of benzonitrile must be made [19]. In this compound the carbon-carbon bond of the ring (if the $C \equiv N$ bond length, as in other compounds, is 1.158 A) has a length of 1.402 A, which differs very little from its length (1.40 A) in another monosubstituted benzene, fluorobenzene [20]; the length of the single bond between the benzene ring

and the nitrile group is 1.419 A. By subtraction of the covalent radius of carbon in the sp state from the bond length we find the covalent radius of carbon in the sp^2 state; it is found to be 0.729 A or, in round figures, 0.73 A.

The absence of the leveling out of bonds in molecules containing alternating multiple bonds, which is proved by exact radiospectroscopic data, is confirmed by all x-ray and electron diffraction investigations of similar substances (Table 2). The length of an ordinary bond in the molecules cited in Table 2 is identical or close to the sum of the covalent radii of carbon in the appropriate valence states, and the lengths of the multiple bonds differ very little from those of bonds in the "nonresonating" molecules of ethylene, acetylene, and hydrocyanic acid.

The central bond in butadiene, formed by two carbon atoms in a state of trigonal hybridization, should be 1.46 A, which is in agreement with the electronographic measurements of Schomaker and Pauling [21]. In a recent paper on the investigation of butadiene [22] the C−C bond length is given the value 1.483 A (which probably requires some correction); the C=C bond length is found to be 1.337, whereas according to recent data the length of the double bond in ethylene is 1.337 A [8] or 1.334 A [23]. Hence, the double bond in butadiene is equal in length to that in ethylene or differs from it only very slightly.

From an examination of the experimental material on bond lengths it follows that open systems having alternating multiple bonds differ in principle from plane cyclic systems in which the movement of π-electrons in the field of all the nuclei ensures the equivalence of all the carbon-carbon bonds, as in benzene, or insignificant departures from the length of carbon-carbon bonds in benzene, as in condensed aromatic hydrocarbons. Quantum-mechanical calculations of different characteristics of molecules with alternating multiple bonds (resonance energies, bond lengths) are based on the assumption that the π-electrons in such molecules are "generalized." As far as experiment shows, the delocalization of π-electrons in open systems having alternating multiple bonds in the ground (unexcited) state is not observed so that quantum-mechanical calculations of the characteristics of such molecules are in principle invalid.

In accordance with the various states of hybridization of the orbitals of carbon atoms the σ-bonds between them should exist as the following six types, whose lengths are determined by the sums of the corresponding covalent radii of carbon:

$$\geq C-C\leq \sigma_{sp^3,\ sp^3} \quad 0{,}77 + 0{,}77 = 1{,}54\ \text{Å}$$

$$\geq C-C= \sigma_{sp^3,\ sp^2} \quad 0{,}77 + 0{,}73 = 1{,}50\ \text{Å}$$

$$\geq C-C\equiv \sigma_{sp^3,\ sp} \quad 0{,}77 + 0{,}69 = 1{,}46\ \text{Å}$$

$$=C-C= \sigma_{sp^2,\ sp^2} \quad 0{,}73 + 0{,}73 = 1{,}46\ \text{Å}$$

$$=C-C\equiv \sigma_{sp^2,\ sp} \quad 0{,}73 + 0{,}69 = 1{,}42\ \text{Å}$$

$$\equiv C-C\equiv \sigma_{sp,\ sp} \quad 0{,}69 + 0{,}69 = 1{,}38\ \text{Å}$$

σ-Bonds of various types are shortened when there is also a π-bond between the carbon atoms. The relation between the length of a $\sigma_{sp^2,\ sp^2}$ bond and the number of π-electrons localized in this bond is given by Pauling's curve in the section from ethylene to graphite. Thus, the $\sigma_{sp^2,\ sp^2}$ bond in ethylene, in which two π-electrons are localized, is shortened to 1.337 A, and in benzene, when one π-electron is localized in the bond, the bond is shortened to 1.397 A. In acetylene the $\sigma_{sp,\ sp}$ bond (1.38 A) is shortened to 1.207 A under the influence of four π-electrons.

Batuev [28], in discussing conjugation in butadiene, estimates the changes in bond lengths from the vibration frequencies of the bonds; he concludes that in conjugated systems, in spite of mesomerism theory, the leveling out of bonds does not occur, and all bonds, single and multiple, are shortened. As regards this approach to the estimation of changes in bond lengths the following must be stated. Insofar as changes in

vibration frequencies of bonds of a definite type depend not only on the mutual effects of electron systems, but also on change in the mechanical picture of the vibration, conclusions about the shortening or lengthening of bonds based on the changes in the characteristic frequencies are not unequivocal. Thus, mechanical factors are the source of the lowering of the vibration frequency of the double bond of deuteroethylene by 12 cm^{-1}; the triple bond of propyne does not differ in length from the triple bond in acetylene, but in the first case the vibration frequency is 2125 cm^{-1}, whereas in the second it is 1965 cm^{-1}. While noting the absence of a leveling out of bonds in molecules containing alternating multiple bonds, Batuev gives no physically based explanation of the considerable shortening of single bonds situated between multiple bonds.

In an examination of the properties of organic molecules, Burawoy [29] concludes that the theory of resonance or mesomerism is in conflict with the facts. The fundamental thesis in this theory is the existence of nonlocalized electrons, which is not confirmed experimentally.

Carbon atoms in different valence states must have different electronegativities. From Gordy's relation [30], $x = 0.31\left(\frac{n+1}{r}\right) + 0.5$, which gives the relation of the electronegativity of an element to the number of valence electrons and the covalent radius, we find that the electronegativity of carbon in a state of trigonal hybridization is 2.62, and that of carbon in a state of linear hybridization is 2.75.

The enhanced electronegativity of carbon in the sp^2 and sp states, as compared with the sp^3 state (2.5), is the main factor leading to a reduction of the dipole moments of functional derivatives of unsaturated and aromatic hydrocarbons, as compared with derivatives of saturated hydrocarbons. For the interpretation of experimental data on the dipole moments of organic compounds there is no need to introduce concepts of the mesomeric effect of halogens and other elements having unshared electron pairs.

SUMMARY

1. The covalent radii of carbon in the sp^2 and sp states are 0.73 and 0.69 A, respectively.

2. The phenomenon of hyperconjugation of the first order (σ, π-conjugation) does not exist. The shortening of a single carbon-carbon bond adjacent to a multiple bond is due not to a displacement of electrons by a hyperconjugational (resonance-mesomerism) mechanism, but to an orbital effect: a reduction in the covalent radii of carbon with increase in the contribution of bonding orbitals of the s type.

3. In molecules containing alternating multiple bonds the delocalization of π-electrons and leveling out of lengths of bonds do not occur. In such molecules the mesomeric (conjugation) effect (static effect of π,π-conjugation) postulated by resonance-mesomerism theory does not appear. The shortening of single bonds observed in molecules containing alternating multiple bonds is due to an orbital effect.

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ACTION OF NUCLEOPHILIC REAGENTS ON COMPOUNDS OF THE TYPE $[Cl(CH_2)_n CCl=]_2$

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The catalytic "hydrodimerization" of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes, which proceeds by the scheme [1, 2]

$$Cl(CH_2)_nCCl_3 \xrightarrow[\text{catalyst}]{H_2} [Cl(CH_2)_nCCl_2-]_2$$

is of interest for the preparation of long-chain molecules. In particular, by the use of this reaction the preparation has been effected of, for example, the normal dicarboxylic acid containing 16 carbon atoms [2], the ω-hydroxy carboxylic acid containing a chain of 15 carbon atoms [3], and some other compounds. The authors of the present paper showed [4] that compounds of the type $[Cl(CH_2)_n CCl_2-]_2$, in which n is even, undergo exchange reactions with nucleophilic reagents with replacement of one or both terminal chlorine atoms in all cases with the exception of those for which n = 2. The hexachlorohexane of structure $(ClCH_2CH_2CCl_2-)_2$ like 1,1,1,3-tetrachloropropane (by the hydrodimerization of which it is synthesized), does not undergo exchange reactions with nucleophilic reagents under the usual conditions.

In the present paper, we describe the action of nucleophilic reagents on compounds of structure $[Cl(CH_2)_nCCl=]_2$, which are prepared both by the direct catalytic hydrogenation of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes [1, 2], and also by the action of zinc on compounds of the type $[Cl(CH_2)_nCCl_2-]_2$. This gives both α,ω-disubstituted dichloroalkenes and monosubstituted trichloroalkenes. Unlike saturated 1,3,3,4,4,6-hexachlorohexane, unsaturated 1,3,4,6-tetrachloro-3-hexene undergoes exchange reactions with nucleophilic reagents, though with greater difficulty than higher compounds of this type. Also, we effected the hydrodimerization of 1,1,1,9-tetrachlorononane, and from 1,9,9,10,10,18-hexachlorooctadecane we prepared several compounds with chains of 18 and 20 carbon atoms.

EXPERIMENTAL

3,4-Dichloro-N,N,N',N'-tetraethyl-3-hexene-1,6-diamine. A solution of 11.0 g (0.05 mole) of 1,3,4,6-tetrachloro-3-hexene and 29.0 g (0.04 mole) of diethylamine in 50 ml of ethanol was heated in a steel test tube at 100° for six hours. The reaction mixture was diluted with three times the amount of water, acidified with hydrochloric acid, and extracted with chloroform. After the removal of neutral products the aqueous solution was made alkaline and extracted with chloroform. We obtained 5 g (34.4%) of substance. Found: MR 84.425 Calculated MR 83.99. Found: N 9.69; 9.67%. $C_{14}H_{28}Cl_2N_2$. Calculated: N 9.49%.

3,4,6-Trichloro-3-hexen-1-ol Acetic Ester. A solution of 12.5 g (0.05 mole) of 1,3,4,6-tetrachloro-3-hexene and 23.0 g (0.23 mole) of calcined potassium acetate in 50 ml of glacial acetic acid was boiled for 18 hours. Acetic acid was distilled off, and the residue was treated with water and extracted with chloroform.

Solvent was distilled off, and drying over sodium sulfate gave 5.9 g (42.2%) of substance; b. p. 107° (2 mm); $n^{20}D$ 1.4930; d^{20}_4 1.2922. Found MR 55.23; calculated MR 54.99. Found %: C 39.30, 39.22; H 4.07, 4.18. $C_9H_{11}Cl_3O_2$. Calculated %: C 39.13; H 4.31%.

5,6-Dichloro-5-decenylene-1,10-bistriethylammonium Diiodide. A solution of 10.0 g (0.04 mole) of 1,5,6,10-tetrachloro-5-decene and 20.8 g (0.2 mole) of diethylamine in 50 ml of ethanol was placed in a 500 ml autoclave tube. The autoclave was heated for 12 hours in a boiling water bath. The reaction mixture was treated with three times the amount of water and acidified with hydrochloric acid. After the extraction of neutral products, the reaction mixture was treated with alkali and extracted with chloroform. We obtained 10 g (62.0%) of substance of b. p. 176-178° (4 mm), and 3.5 g (0.009 mole) of this 5,6-dichloro-N,N,N',N'-tetraethyl-5-decene-1,10-diamine was heated at 90° for 12 hours with 6.2 g (0.4 mole) of ethyl iodide in 20 ml of ethanol. Ethanol was distilled off, and the residue was crystallized from hot alcohol. We obtained 3.0 g (48.3%) of substance of m. p. 233.5-234°. Found %: C 39.65, 39.64; H 6.80, 6.89; total halogen 48.72; 48.35; N 4.12; 4.33. $C_{22}H_{46}Cl_2I_2N_2$. Calculated %: C 39.85; H 6.99, total halogen 49.00; N 4.22%.

5,6-Dichloro-1,10-diethoxy-5-decene. In small portions 27.8 g (0.1 mole) of 1,5,6,10-tetrachloro-5-decene was added to a solution of sodium ethoxide (0.21 mole) prepared from 5.0 g of sodium in 85 ml of absolute ethanol. The reaction mixture was heated for six hours at 120°. We obtained 26.2 g (88.2%) of substance; b. p. 145° (3 mm); $n^{20}D$ 1.4750, d^{20}_4 1.0511. Found: MR 79.35; calculated MR 79.40. Found %: C 56.63, 56.54; H 7.91, 8.20. $C_{14}H_{28}Cl_2O_2$. Calculated %: C 56.56; H 8.82.

5,6,10-Trichloro-5-decen-1-ol Acetic Ester. A solution of 15.0 g (0.05 mole) of 1,5,6,10-tetrachloro-5-decene, 21.0 g (0.2 mole) of calcined potassium acetate, and 0.1 g of potassium iodide in 100 ml of glacial acetic acid was heated at 140° for 40 hours. Acetic acid was distilled off, and the residue was treated with three times the amount of water and extracted with chloroform. Drying over sodium sulfate and distillation of solvent gave 10.1 g (60.0%) of substance; b. p. 146° (2 mm); $n^{20}D$ 1.4890, d^{20}_4 1.1844. Found: MR 73.40; calculated MR 73.40. Found %: C 48.06, 48.00; H 6.31, 6.31. $C_{12}H_{19}Cl_3O_2$. Calculated %: C 47.78; H 6.34.

7,8-Dichloro-1,14-diethoxy-7-tetradecene. A mixture of 3 g (0.13 mole) of sodium in 50 ml of absolute ethanol and 16.7 g (0.07 mole) of 1,7,8,14-tetrachloro-7-tetradecene was boiled for six hours. This gave 15.1 g (86.2%) of substance; b. p. 168-170° (2 mm); $n^{20}D$ 1.4699, d^{20}_4 1.0052. Found: MR 98.07; calculated MR 97.88. Found %: C 61.06, 61.06; H 9.66, 9.61. $C_{18}H_{34}Cl_2O_2$. Calculated %: C 61.18; H 9.70.

6,7-Dichloro-N,N,N',N'-tetraethyl-7-tetradecene-1,14-diamine. A solution of 15.0 g (0.05 mole) of 1,7,8,14-tetrachloro-7-tetradecene and 13 ml (0.13 mole) of diethylamine in 50 ml of ethanol was placed in a 500 ml autoclave tube. The autoclave was heated for five hours in a boiling water bath. The reaction mixture was treated with water and acidified with hydrochloric acid. After extraction of neutral products the reaction mixture was treated with alkali and extracted with chloroform. We obtained 9.0 g (50.0%) of substance, b. p. 202° (1 mm). The base was a very viscous liquid. Found %: C 64.45; H 10.62; Cl 17.96; N 6.92. $C_{22}H_{44}Cl_2N_2$. Calculated %: C 64.84; H 10.88; Cl 17.40; N 6.87.

Hydrogenation of 1,1,1,9-Tetrachlorononane. A solution of 6.8 g (0.4 mole) of ammonia in 110 ml of methanol and 106 g (0.4 mole) of 1,1,1,9-tetrachlorononane were added to previously reduced palladium oxide (6 g of 5% $Pd/BaSO_4$) in 50 ml of methanol containing 2 ml of glacial acetic acid. The hydrogenation was carried out in a glass hydrogenation flask at atmospheric pressure. After ten hours the absorption of hydrogen stopped. In all, 4.5 liters of hydrogen was absorbed. The catalyst was filtered off and washed with water and chloroform; the chloroform layer was dried over calcium chloride. After distillation of the chloroform we obtained 47.5 g (51.7%) of 1,9,9,10,10,18-hexachlorooctadecane, m. p. 55.5-56° (from a mixture of alcohol and acetone). Found %: C 46.56, 46.88; H 6.96, 7.05; Cl 46.70. $C_{18}H_{32}Cl_6$. Calculated %: C 46.88; H 6.99; Cl 46.13. In addition we isolated 10 g of nonyl chloride; b. p. 55-56° (1 mm); $n^{20}D$ 1.4369; d^{20}_4 0.8785. Found: MR 48.25, calculated MR 48.63. Found: C 66.42; 66.50; H 11.43; 11.44; Cl 22.61; 22.38%. $C_9H_{19}Cl$. Calculated: C 66.43; H 11.77; Cl 21.79%. For nonyl chloride the literature [5] gives: b.p. 76° (4 mm); n^{20}_D 1.4400; d^{20}_4 0.8803.

1,9,10,18-Tetrachloro-9-octadecene. Gradual addition was made of 22.6 g (0.05 mole) of 1,9,9,10,10,18-hexachlorooctadecane to a stirred suspension of 6 g (0.09 mole) of zinc dust in 100 ml of absolute alcohol (the zinc was activated by heating it with 0.2 ml of glacial acetic acid and 0.2 ml of hydrobromic acid). The reaction occurred with slight evolution of heat. After being heated for four hours at 100°, the mixture was cooled and

filtered from excess of zinc; the filtrate was acidified with dilute hydrochloric acid, treated with water, and extracted with chloroform. Vacuum distillation gave 15.8 g (85%) of substance; b. p. 190-191° (1 mm); $n^{20}D$ 1.4935, d^{20}_4 1.0916; Calculated MR 104.27; calculated MR 104.26. Found %: C 55.46, 55.34; H 8.20, 8.19; Cl 36.45, 36.48. $C_{18}H_{32}Cl_4$. Calculated %: C 55.39; H 8.26; Cl 36.33.

10,11-Dichloro-10-eicosenedioic Acid. A solution of 4.9 g (0.1 mole) of sodium cyanide and 0.1 g of potassium iodide in 10 ml of water was added to a solution of 10 g (0.025 mole) of 1,9,10,18-tetrachloro-9-octadecene in 70 ml of 2 ethoxytthanol. The reaction mixture was heated at 120° for six hours. 2-Ethoxyethanol was distilled off, and the mixture was treated with water and extracted with chloroform. After the removal of chloroform we obtained 8.5 g (89.4%) of substance; b. p. 234° (1 mm); $n^{20}D$ 1.4880, d^{20}_4 1.0374; Found MR 103.27. $C_{20}H_{32}Cl_2O_2$. Calculated MR 102.91.

The product was hydrolyzed by boiling it with 25 ml of glacial acetic acid and 25 ml of concentrated hydrochloric acid for five hours. On treatment of the reaction mixture with water there was 6.5 g of precipitate, which was crystallized from heptane; m. p. 84°; yield 71.0%. Found %: C 58.35, 58.21; H 8.36, 8.17. $C_{20}H_{32}Cl_2O_4$. Calculated %: C 58.68; H 8.37.

9,10,18-Trichloro-9-octadecen-1-ol. Addition was made of 10 g (0.1 mole) of calcined potassium acetate and 0.1 g of potassium iodide to a solution of 10 g (0.025 mole) of 1,9,10,18 tetrachloro-9-octadecene in 70 ml of glacial acetic acid. The reaction mixture was heated at 120° for 24 hours. Acetic acid was distilled off, and the residue was treated with water and extracted with chloroform. We obtained 9.0 g of substance of b. p. 214° (1.5 mm), and 5.0 g of this was subjected to alcoholysis by boiling it with 50 ml of methanol and 0.5 ml of concentrated hydrochloric acid for six hours. Methanol was distilled off, and the operation was repeated with 25 ml of methanol and 0.25 ml of concentrated hydrochloric acid; the reaction mixture was then treated with water and extracted with chloroform. We obtained 3.95 g (82%) of substance; b. p. 202° (2 mm); $n^{20}D$ 1.4941; d^{20}_4 1.0708. Found MR 101.08; calculated MR 100.98. Found %: C 57.65, 57.86; H 8.70, 8.78. $C_{18}H_{33}Cl_3O$. Calculated %: C 58.14; H 8.94.

SUMMARY

1. By the hydrogenation of 1,1,1,9-tetrachlorononane over palladium, 1,9,9,10,10,18-hexachlorooctadecane was synthesized. Under the action of zinc this hexachloro compound gave 1,9,10,18-tetrachloro-9-octadecene.

2. Reaction of nucleophilic reagents with compounds of the type $[Cl(CH_2)_nCCl=]_2$ gave the compounds $X(CH_2)_nCCl=CCl(CH_2)_nCl$ (n = 2, 4, and 8) and $X(CH_2)_nCCl=CCl(CH_2)_nX (n=4,6)$ $X=CH_3COO$, OH, $(C_2H_5)_2N$, CN, COOH, $(C_2H_5)_3NI$.

3. 1,3,4,6-Tetrachloro-3-hexene, unlike the saturated 1,3,3,4,4,6-hexachlorohexane and 1,1,1,3-tetrachloropropane, undergoes exchange reactions with nucleophilic reagents, but these reactions proceed less readily than those with higher tetrachloroalkenes.

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ACTION OF SULFUR, SELENIUM, AND SULFUR CHLORIDES ON TRIALKYLALUMINUMS

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In continuation of our investigation of the reactions of organoaluminum compounds * we have now studied the action of sulfur, selenium, and sulfur chlorides on trialkylaluminums. Depending on the experimental conditions and the relative amounts of reactants, the reaction of organomagnesium compounds with sulfur leads to thiols, disulfides, and polysulfides. Wuyts [2-4] explains the formation of thiols and disulfides by the following schemes:

$$RMgX + S \longrightarrow RSMgX \xrightarrow{H_2O} RSH,$$

$$2RSMgX + S \longrightarrow R_2S_2 + S(MgX)_2,$$

and the observed formation of sulfide in the case of phenylmagnesium bromide he explains by the secondary reaction:

$$R_2S_2 + RMgX \longrightarrow R_2S + RSMgX.$$

We studied the reaction of trialkylaluminums with sulfur for the case of triethyl-, triisobutyl-, and tripropylaluminums in absence of solvents. The relative amounts of reactants substantially affected the course of the reaction and the yields of products. The reaction of one g-atom of sulfur with one mole of trialkylaluminum proceeded unequivocally in accordance with the scheme:

$$R_3Al + S \longrightarrow R_2AlSR \xrightarrow{H_2O} RSH,$$

in which R = C_2H_5, n-C_3H_7, i-C_4H_9. The addition of sulfur proceeded at 40-60°. The resulting R_2AlSR (R = C_2H_5, i-C_4H_9) was vacuum-distilled without decomposition, and under the action of water it gave the corresponding thiol. With a ratio of two g-atoms of sulfur to one mole of trialkylaluminum the second half of the sulfur taken for reaction added only at 90-100°. The course of the reaction was complex, and a mixture of products was obtained. The second atom of sulfur did not react similarly to the first, i.e., reaction did not lead to the formation of $RAl(SR)_2$. On fractionation of the reaction mixture, which was carried out in the case of triethyl- and triisobutyl-aluminums, the products were the corresponding sulfide R_2S, disulfide R_2S_2, and dialkyl (alkylthio)aluminum R_2AlSR, together with a nondistilling solid residue which, on treatment with dilute hydrochloric acid, yielded a hydrocarbon (ethane or isobutane) and hydrogen sulfide. Decomposition of the reaction mixture with water gave thiol, sulfide, disulfide, hydrogen sulfide, and hydrocarbon (sulfur was not liberated).

* For preceding communication see [1].

Hence, the reaction of trialkylaluminums with two atomic proportions of sulfur goes in accordance with the following scheme:

$$R_3Al + 2S \longrightarrow RSR + RSSR + R_2AlSR + R_nAl_mS_q$$
$$\downarrow H_2O \qquad \downarrow H_2O$$
$$R = C_2H_5, \quad i\text{-}C_4H_9 \qquad 2RH + RSH \quad nRH + qH_2S$$

The mechanism of the formation of sulfide and disulfide in this reaction is not altogether clear. On the assumption that the reaction proceeds stagewise via the intermediate formation of R_2AlSR, the action of sulfur on this compound ($R = i\text{-}C_4H_9$) was investigated. It was found that with a ratio of R_2AlSR to sulfur of 2:1 one-half of the R_2AlSR taken was recovered unchanged, i.e., reaction does not occur in accordance with an equation analogous to that given by Wuyts for organomagnesium compounds:

$$2RSAlR_2 + S \not\longrightarrow R_2S_2 + R_2Al-S-AlR_2$$

The reaction products in this case are sulfide and disulfide. The action of one g-atom of sulfur on one mole of R_2AlSR gives the same result as the action of two g-atoms of sulfur on one mole of R_3Al; some of the R_2AlSR is recovered unchanged:

$$RSAlR_2 + S \longrightarrow RSR + RSSR + R_nAl_mSq$$

When decomposed with dilute hydrochloric acid, the solid nondistilling residue R_n, Al_m, S_q evolves only isobutane and hydrogen sulfide. No liberation of sulfur occurs, which indicates the absence of Al−S−S−Al linkages. From the amounts of sulfide and disulfide obtained it follows that to a certain extent they are formed also by the involvement of part of the remaining Al−C bonds in the reaction (more than two-thirds of one of the two Al−C bonds in R_2AlSR enters the reaction).

We consider it probable that the reaction of sulfur with R_2AlSR proceeds via the formation of the alkyldithio derivative R_2AlSSR, which is further transformed into the disulfide:

$$R_2AlSR + S \longrightarrow R_2AlSSR \longrightarrow R_2S_2 + R_nAl_mS_q$$

To a certain extent this view is supported by the reaction of sodium isobutyl sulfide with sulfur, which we have studied. On addition of one g-atom of sulfur to a solution of one mole of sodium isobutyl sulfide in absolute alcohol, rapid dissolution of sulfur occurs, and on subsequent heating there is a precipitate of Na_2S_2 and the disulfide is formed in quantitative yield. When the reaction is carried out with one-half of the amount of sulfur, only one-half of the sodium isobutyl sulfide reacts. The reaction appears to proceed through the disulfide stage:

$$2i\text{-}C_4H_9SNa + 2S \longrightarrow 2i\text{-}C_4H_9SSNa \longrightarrow (i\text{-}C_4H_9)_2S_2 + Na_2S_2$$

As regards the formation of sulfide in the reaction of sulfur with trialkylaluminum, we may make the following observations. Although we have found that R_3Al reacts with disulfides in accordance with the scheme

$$R_3Al + R_2S_2 \longrightarrow R_2S + R_2AlSR,$$

in which $R = i\text{-}C_4H_9$, this reaction cannot occur in the reaction of sulfur with trialkylaluminum, for it follows from the results cited above that sulfide is formed by the action of sulfur on $RSAlR_2$ and that no trialkylaluminum is to be found in the reaction mixture after the reaction of the first atomic proportion of sulfur. Under the conditions investigated (110-120°) reaction between disulfide and R_2AlSR, which could lead to the formation of sulfide, e.g., in accordance with the scheme

$$R_2AlSR + R_2S_2 \longrightarrow R_2S + RAl(SR)_2,$$

does not occur. Only with prolonged heating at a higher temperature (140-160°) is a very small amount of sulfide ($R = i\text{-}C_4H_9$) formed.

In the reaction of sulfur with R_3Al in the ratio 3:1, after decomposition of the reaction mixture we obtained sulfide, disulfide, trisulfide, hydrocarbon, and hydrogen sulfide. No thiol was detected. Hence, in this case reaction proceeds by the scheme:

$$R_3Al+3S \longrightarrow R_2S+R_2S_2+R_2S_3+R_nAl_mS_q \xrightarrow{\downarrow H_2O} nRH+qH_2S$$

in which R = i-C_4H_9.

From the amount of sulfide, disulfide, and trisulfide liberated it follows that more than two Al—C bonds in R_3Al take part in the reaction. The reaction of selenium with trialkylaluminums was studied for the cases of triethyl- and triisobutyl-aluminums. Selenium begins to react appreciably with trialkylaluminums at about 70-80°. A second and third selenium atom can be caused to add only at temperatures of 140-150°. After decomposition with water the products of the reaction of one g-atom of selenium with one mole of triethyl- or triisobutyl-aluminum gave only the corresponding selenol, hydrogen selenide, and the hydrocarbon, i.e., reaction occurred according to the scheme:

$$R_3Al+Se \longrightarrow R_2AlSeR \xrightarrow{H_2O} 2RH+RSeH,$$

in which R = C_2H_5; i-C_4H_9. With a ratio of selenium to trialkylaluminum of 2:1, together with the selenols we isolated the corresponding selenides and diselenides and, unlike the case of sulfur, the main reaction product was the selenide:

$$R_3Al+2Se \xrightarrow[H_2O]{\Delta} RSeH+R_2Se+R_2Se_2+RH,$$

in which R = C_2H_5; i-C_4H_9. Finally, with a ratio of selenium to trialkylaluminum of 3:1 the main product was diselenide; the selenol and selenide were formed also.

We studied the reaction of trialkylaluminums with sulfur chlorides for the case of triisobutylaluminum. Sulfur chloride react very vigorously with R_3Al, even in heptane solution, and much sulfur is liberated. Reaction can be carried out smoothly with an ethereal solution of triisobutylaluminum at from − 30° to + 20°, and at the start of the addition of sulfur chlorides the temperature is kept as low as possible. On reaction of sulfur dichloride with triisobutylaluminum at a ratio of 1:1.5 under the conditions indicated, after decomposition of the reaction mixture we isolated almost equal amounts of diisobutyl sulfide and diisobutyl disulfide, and with stoichiometric proportions of the reactants we obtained also a little of the corresponding trisulfide:

$$R_3Al+SCl_2 \longrightarrow R_2S+R_2S_2+R_2S_3,$$

in which R = i-C_4H_9.

On reaction of disulfur dichloride with a small excess (over the stoichiometric amount) of triisobutylaluminum, after decomposition of the reaction mixture we isolated the corresponding sulfide, disulfide, and trisulfide, together with a little of a higher-boiling fraction:

$$R_3Al+S_2Cl_2 \longrightarrow R_2S+R_2S_2+R_2S_3+R_2S_x,$$

in which R = i-C_4H_9. Neither in the reaction with sulfur dichloride, nor in the reaction with disulfur dichloride, was isobutyl chloride detected.

EXPERIMENTAL

Reaction of Triisobutylaluminum with Sulfur. 1. a) In small portions 9 g (0.281 mole) of sulfur was added in an atmosphere of pure nitrogen with vigorous stirring to 56 g (0.282 mole) of triisobutylaluminum.

With the heat of reaction the temperature rose to 50-60° and remained at this level for one hour. After the addition of the whole of the sulfur the mixture was heated at 100° for 15 minutes. The reaction product was vacuum-distilled. We obtained 56 g (86%) of $i\text{-}C_4H_9SAl(i\text{-}C_4H_9)_2$, b. p. 155° (1 mm). Found %: C 61.70, 61.71; H 11.66, 11.80; S 13.38, 13.33. $C_{12}H_{27}AlS$. Calculated %: C 62.56; H 11.81; S 13.93. A 7.46-g portion of the $i\text{-}C_4H_9SAl(i\text{-}C_4H_9)_2$ was decomposed by addition of alkali to the solution. We obtained 2.75 g (94%) of 2-methyl-1-propanethiol; b. p. 87-88°; $n^{20}D$ 1.4385, d^{20}_4 0.8348; found MR 28.38; calculated MR 28.36. The literature [5] gives: b. p. 88°; $n^{20}D$ 1.4386, d^{20}_4 0.8357.

b) Under similar conditions from 24.5 g (0.124 mole) of triisobutylaluminum and 3.95 g (0.124 mole) of sulfur with subsequent decomposition of the reaction mixture with methanol and hydrochloric acid at 0-10°, we isolated 9.5 g (85%) of 2-methyl-1-propanethiol.

2. a) In small portions 11.1 g (0.344 mole) of sulfur was added with stirring to 34.5 g (0.174 mole) of triisobutylaluminum. One-half of the sulfur taken reacted with triisobutylaluminum at 50-60°, and the remainder only at 90-120°. The whole operation took one hour, and the mixture was then heated with stirring for two hours at 120°. Fractionation of the mixture gave 2.6 g of diisobutyl sulfide; b. p. 62° (13 mm); $n^{20}D$ 1.4485, d^{20}_4 0.8293; found MR 47.30, calculated MR 47.06 (the literature [6] gives $n^{20}D$ 1.4468, d^{20}_4 0.8263). Also 11.5 g of diisobutyl disulfide; b. p. 91-92° (13 mm); $n^{20}D$ 1.4870, d^{20}_4 0.9120; found MR 55.24; calculated MR 54.98; (the literature [6] gives b. p. 215°; $n^{20}D$ 1.4866, d^{20}_4 0.9090). Also 7.5 g of $(i\text{-}C_4H_9)_2AlS-C_4H_9$, b. p. 165-168° (3 mm), by the decomposition of which 2.1 g of 2-methyl-1-propanethiol was isolated. The nondistilling infusible residue amounted to 10.8 g, and by the decomposition of this with hydrochloric acid isobutane and hydrogen sulfide were liberated.

b) In a similar manner, but with subsequent decomposition of the reaction product with water and hydrochloric acid and the usual treatment, from 17.5 g (0.088 mole) of triisobutylaluminum and 5.6 g (0.175 mole) of sulfur we obtained, after decomposition, 1.5 g of 2-methyl-1-propanethiol, 1.5 g of diisobutyl sulfide, and 7 g of diisobutyl disulfide.

3. Similarly, to 13.5 g (0.069 mole) of triisobutylaluminum 6.5 g (0.203 mole) of sulfur was added. Toward the end of the reaction the temperature was raised for a short time to 150°. When the reaction product cooled, it formed a thick white mass, which was decomposed with dilute hydrochloric acid at 10-15°. In the decomposition the evolution of isobutane and hydrogen sulfide was observed. We isolated 11.5 g of substance, from which, after distillation, we obtained 4 g of diisobutyl sulfide, 2.8 g of diisobutyl disulfide, 2 g of diisobutyl trisulfide (b. p. 78-80° (1 mm); $n^{20}D$ 1.5255, d^{20}_4 1.0031; found MR 64.34; calculated MR 64.52) and a residue (about 3 g).

Reaction of Tripropylaluminum with Sulfur. In small portions 4.8 g (0.15 mole) of sulfur was added with vigorous stirring to 23.6 g (0.15 mole) of tripropylaluminum. The temperature was maintained at 40-50° by the heat of reaction. After the usual treatment we isolated 8.1 g (71%) of 1-propanethiol; b. p. 67-68°, $n^{20}D$ 1.4363, d^{20}_4 0.8358; found MR 23.81; calculated MR 23.74 (the literature [5] gives: b. p. 67°, $n^{25}D$ 1.4351, d^{25}_4 0.8357.

Reaction of Triethylaluminum with Sulfur. In small portions 8.4 g (0.263 mole) of ground stick sulfur was added to 30 g (0.263 mole) of triethylaluminum. Up to 30° no appreciable reaction was observed. The reaction was carried out at 60-80° for 90 minutes. The reaction product was a liquid, and distillation of this gave 32 g of diethyl(ethylthio)aluminum, b. p. 104° (1 mm). Found %: C 49.48, 49.71; H 10.39, 10.46; Al 18.44, 18.30. $C_6H_{15}AlS$. Calculated %: C 49.32; H 10.27; Al 18.46.

Reaction of Diethyl(ethylthio)aluminum with Sulfur. Sulfur (2.6 g, 0.081 mole) was added to 12 g (0.08 mole) of diethyl(ethylthio)aluminum with stirring at 100-110°. After the addition of the whole of the sulfur the mixture was heated for one hour at 160-170°. The reaction product was a white solid, the fractionation of which gave: 0.8 g of diethyl sulfide; b. p. 91-93°; $n^{20}D$ 1.4445 (the literature [6] gives: b. p. 92°; $n^{20}D$ 1.44235) [the sulfone, prepared by the oxidation of this substance with hydrogen peroxide in acetic acid, had m. p. 70° (from ether); the literature [7] gives m. p. 72° for $(C_2H_5)_2SO_2$]; also 3 g of diethyl disulfide; b. p. 152-153°; $n^{20}D$ 1.5050, d^{20}_4 0.9898 (the literature [6] gives b. p. 152°; $n^{20}D$ 1.50704, d^{20}_4 0.9920); we isolated also 2 g of diethyl(ethylthio)aluminum and a nondistilling solid residue, which by decomposition first with alcohol and then with hydrochloric acid gave ethane and hydrogen sulfide.

Action of Sulfur on Diisobutyl(isobutylthio)aluminum. a) In small portions 3 g (0.094 mole) of sulfur was added to 43.5 g (0.188 mole) of i-$C_4H_9SAl(i\text{-}C_4H_9)_2$ at 100-110°. The reaction mixture formed a thick white liquid. On distillation we obtained 1 g of diisobutyl sulfide, b. p. 168-170°, and 7.7 g of diisobutyl disulfide, b. p. 62-63° (1 mm), $n^{20}D$ 1.4875, d^{20}_4 0.9120; we also obtained 23.3 g of i-$C_4H_9SAl(i\text{-}C_4H_9)_2$, b. p. 152-155° (1 mm). On decomposition with alcohol and hydrochloric acid the solid residue (10.5 g) liberated isobutane and hydrogen sulfide.

b) Similarly, from 39.4 g (0.171 mole) of i-$C_4H_9SAl(i\text{-}C_4H_9)_2$ and 5.3 g (0.168 mole) of sulfur we obtained 2 g of diisobutyl sulfide, 14 g of diisobutyl disulfide, 13.3 g of i-$C_4H_9SAl(i\text{-}C_4H_9)_2$, and 12.8 g of a nondistilling solid, in the decomposition of which isobutane and hydrogen sulfide were liberated.

Action of Sulfur on Sodium Isobutyl Sulfide. a) To 7.55 g (0.0675 mole) of i-C_4H_9SNa dissolved in 30 ml of absolute alcohol we added 2.16 g (0.0675 mole) of sulfur, which readily dissolved at room temperature. After distillation of alcohol we isolated 5.7 g (94%) of diisobutyl disulfide, b. p. 92° (13 mm) and $n^{20}D$ 1.4878. The nondistilling yellow solid residue was found to be Na_2S_2.

b) To 15.7 g (0.14 mole) of i-C_4H_9SNa dissolved in 50 ml of absolute alcohol was added 2.24 g (0.07 mole) of sulfur in small portions which readily dissolved at room temperature. On boiling for one hour at the boiling point of alcohol there was a yellow precipitate of Na_2S_2. Alcohol was distilled off at 77-78°. From the residue at 90-95° (14 mm) we isolated 5.6 g (90%) of diisobutyl disulfide, $n^{20}D$ 1.4872 and d^{20}_4 0.9109. No other fractions were found. The solid residue was unchanged i-C_4H_9SNa and Na_2S_2.

Reaction of Triisobutylaluminum with Diisobutyl Disulfide. Diisobutyl disulfide (10.5 g) was added over a period of 20 minutes with stirring to 13 g of triisobutylaluminum; the temperature rose to 55° with the heat of the reaction. The mixture was heated further at 140° for one hour and was then vacuum-distilled. This gave 6.5 g of diisobutyl sulfide, 2 g of diisobutyl disulfide, and 10.1 g of diisobutyl (isobutylthio) aluminum, by the decomposition of which 3.8 g of 2-methyl-1-propanethiol was isolated.

Reaction of Diisobutyl(isobutylthio)aluminum with Diisobutyl Disulfide. A mixture of 19 g of i-$C_4H_9SAl(i\text{-}C_4H_9)_2$, which distilled at 156-157° (2 mm), and 11.2 g of diisobutyl disulfide, b. p. 89-90° (12 mm) and $n^{20}D$ 1.4875, was prepared in a small flask fitted with reflux condenser and previously filled with pure nitrogen. The mixture was heated at 140-160° for ten hours. Fractionation gave 0.5 g of a substance of b. p. 61-63° (13 mm) and $n^{20}D$ 1.4499 [for $(i\text{-}C_4H_9)_2S$ $n^{20}D$ 1.4466 [6]], also 10.2 g of diisobutyl disulfide, 17.8 g of diisobutyl (isobutylthio)aluminum, and a little white solid residue.

Reaction of Triethylaluminum with Selenium. a) Selenium (10.2 g, 0.129 mole) was ground to about 100 mesh and transferred from a small flask through a rubber tube in small portions into 14.7 g (0.129 mole) of triethylaluminum with vigorous stirring. Appreciable reaction could be detected only at about 80°. The reaction product was a slightly turbid liquid, and after its careful decomposition we isolated 10 g (71%) of ethaneselenol; b. p. 52-53°, $n^{20}D$ 1.4830, d^{20}_4 1.3380. The literature [8] gives: b. p. 53.5°, $n^{24}D$ 1.47715; d^{24}_4 1.3954. Found %: C 21.78, 21.81; H 5.82, 6.17. $C_2H_{10}Se$. Calculated %: C 22.03; H 5.54. On decomposition of the reaction product, apart from ethane, the liberation of hydrogen selenide was noted.

b) Similarly, 12 g (0.152 mole) of selenium was added to 9 g (0.79 mole) of triethylaluminum. The first half of the selenium reacted at 80° over a period of one hour. The remaining selenium was caused to add at 140-150° in the course of three hours. After the decomposition we isolated 1.7 g of ethaneselenol, b. p. 52-54°, and 5.4 g of diethyl selenide; b. p. 107-108°; $n^{20}D$ 1.4813, d^{20}_4 1.2144. The literature [9] gives: b. p. 108°; $n^{20}D$ 1.4768, d^{20}_4 1.230. Found %: C 34.95, 35.21; H 7.37, 7.41. $C_4H_{10}Se$. Calculated %: C 35.04; H 7.43. When the reaction product was decomposed with water, much hydrogen selenide was liberated.

Reaction of Selenium with Triisobutylaluminum. a) Slowly, in small portions, 7.9 g (0.101 mole) of selenium was added to 20 g (0.101 mole) of triisobutylaluminum at 70-80° over a period of three hours. After the addition of the whole of the selenium the flask was heated to 150° and stirring was continued for one hour. At the end of the reaction the reaction mixture formed a thick white mass. After decomposition with dilute hydrochloric acid, we isolated 8.9 g of 2-methyl-1-propaneselenol; b. p. 103-104°, $n^{20}D$ 1.4735, d^{20}_4 1.2301. Found %: C 35.17; H 7.44. $C_4H_{10}Se$. Calculated %: C 35.04; H 7.43. In the decomposition, apart from isobutane, the liberation of hydrogen selenide was noted.

b) In small portions 15.8 g (0.2 mole) of selenium was added with continuous stirring to 20 g (0.101 mole) of triisobutylaluminum. The first half of the selenium reacted at 60-80°, and the remainder added only at 120-140°. The whole reaction was carried out in the course of four hours, in the course of which the elimination of a little isobutene was noted. When the reaction product was cool, it was suspended in 50 ml of ether and decomposed at about 10° by the slow addition of dilute hydrochloric acid. The liberation of hydrogen selenide was then noted. We isolated 13.5 g of a mixture of reaction products, by the distillation of which we obtained 5 g of 2-methyl-1-propaneselenol, b. p. 103-104°, 7 g of diisobutyl selenide [b. p. 184-185°, 80-81° (25 mm); $n^{20}D$ 1.4706, d^{20}_4 1.0859. Found %: C 49.32, 49.38; H 8.22, 8.13. $C_8H_{18}Se$. Calculated %: C 49.48; H 9.34], and about 1.5 g of a substance of b. p. above 190° (evidently diisobutyl diselenide).

c) Under analogous conditions 17.3 g (0.22 mole) of selenium was added to 15 g (0.075 mole) of triisobutyl aluminum. The last two-thirds of the selenium added only at 140-150°. The whole reaction took four hours. The reaction product was a white solid mass and was decomposed with a 25% solution of sulfuric acid with heating to 100°. The liberation of much hydrogen selenide was noted. The weight of crude product was 18 g. After distillation we obtained 1.3 g of 2-methyl-1-propaneselenol, b. p. 103-105°, 2.6 g of diisobutyl selenide, b. p. 80-81° (25 mm), 11 g of diisobutyl diselenide [orange liquid; b. p. 134-135° (25 mm); $n^{20}D$ 1.5351, d^{20}_4 1.3751. Found %: C 35.12, 35.18; H 6.77, 6.86. $C_8H_{18}Se$. Calculated %: C 35.30; H 6.66] and about 3 g of residue.

Reaction of Triisobutylaluminum with Sulfur Dichloride. a) A solution of 22 g (0.21 mole) of sulfur dichloride in 50 ml of ether was added slowly to 43 g (0.21 mole) of $Al(i\text{-}C_4H_9)_3$ in 110 ml of ether. The temperature was kept between − 20° and − 30°. The solution of sulfur dichloride was decolorized instantaneously. Decomposition of the reaction product was carried out with hydrochloric acid solution. After the removal of ether, 21 g of crude product was separated, and by fractionation of this we isolated 9.5 g of diisobutyl sulfide [b. p. 63-64° (16 mm); $n^{20}D$ 1.4475, d^{20}_4 0.8280], 8.5 g of diisobutyl disulfide [b. p. 93-94° (14 mm); $n^{20}D$ 1.4855], and about 2 g of higher-boiling fractions.

b) A solution of 27 g (0.262 mole) of sulfur dichloride in 50 ml of ether was added slowly at from 10° to − 20° over a period of one hour to 35 g (0.176 mole) of triisobutylaluminum in 110 ml of ether. After the decomposition and the usual treatment we obtained 29 g of crude product, from which we isolated 10.3 g of diisobutyl sulfide, b. p. 167-168° and $n^{20}D$ 1.4482, 12.6 g of diisobutyl disulfide, b. p. 66-67° (1 mm) and $n^{20}D$ 1.4872, and 5 g of diisobutyl trisulfide, b. p. 86-87° (2 mm) and $n^{20}D$ 1.5264.

Reaction of Triisobutylaluminum with Disulfur Dichloride. A solution of 35 g (0.25 mole) of disulfur dichloride in 40 ml of ether was added slowly at 10-20° to 49.6 g (0.25 mole) of triisobutylaluminum in 125 ml of ether. After the usual treatment and distillation of ether we obtained 32 g of crude fraction, and the fractionation of this gave: 7 g of diisobutyl sulfide (b. p. 168-170°; $n^{20}D$ 1.4485; d^{20}_4 0.8283; found MR 47.22; calculated MR 47.06), 8 g of diisobutyl disulfide [b. p. 63-64° (1 mm); $n^{20}D$ 1.4862; d^{20}_4 0.9185. Found %: C 53.27, 53.35; H 10.02, 0.99. $C_8H_{18}S_2$. Calculated %: C 53.39; H 10.17]. 14 g of diisobutyl trisulfide [b. p. 82-83° (2 mm); $n^{20}D$ 1.5248; d^{20}_4 1.0029. Found %: C 45.64, 45.75; H 8.61, 8.82. $C_8H_{18}S_3$. Calculated %: C 45.66; H 8.62], and about 3 g of residue.

SUMMARY

1. The action of sulfur, selenium, and sulfur chloride on trialkylaluminums was studied.

2. In the reaction of one g-atom of sulfur with one mole of trialkylaluminum the dialkyl(alkylthio) aluminum is formed; in the reaction of two and more g-atoms of sulfur with one mole of trialkylaluminum the main reaction products are the corresponding disulfides, sulfides, and polysulfides; products of structure $RAl(SR)_2$ and $Al(SR)_3$ are not formed.

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2-CYCLOPENTEN-1-YLPHOSPHONIC ESTERS AND SOME OF THEIR DERIVATIVES

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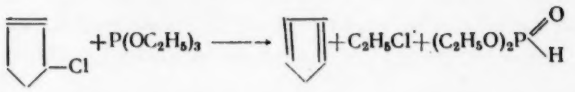
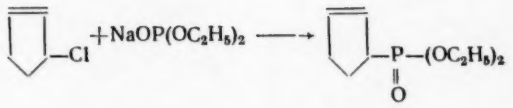
In connection with the investigations that we have carried out on organic derivatives of phosphorus containing the cyclopentene and cyclohexene rings, and also on their epoxy derivatives [1], it was desirable to prepare cyclopentenylphosphonic esters with the double bond in a different position in the ring and to obtain the corresponding epoxides. With this object we carried out experiments on the action of trialkyl phosphites and of sodium dialkyl phosphites on 3-chlorocyclopentene. The action of triethyl phosphite on 3-chlorocyclopentene did not give the desired result. At low temperatures the reaction did not go. At 120° there occurred the quantitative formation of cyclopentadiene by the elimination of hydrogen chloride, which with triethyl phosphite gave ethyl chloride and diethyl hydrogen phosphite:



The reaction of 3-chlorocyclopentene with sodium diethyl phosphite gave the expected cyclopentenylphosphonic ester:



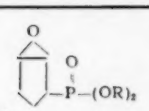
Other 2-cyclopenten-1-ylphosphonic esters were prepared analogously. Their constants are given in Table 1.

TABLE 1

R =	B. p. in °C (p in mm)	n_D^{20}	d_0^{20}	*MR* found	*MR* calculated	Yield %
Diethyl	100—100,5 (3)	1,4579	1,0726	51,94	51,96	74
Dipropyl	110—110,5 (1,5)	1,4553	1,0235	60,21	61,20	38,5
Diisopropyl	96— 96,5 (2)	1,4483	1,0176	59,75	61,20	31,0
Dibutyl	122—123 (1)	1,4544	1,0053	70,18	70,43	30,0
Diisobutyl	126,5—127 (4)	1,4531	0,9990	70,45	70,43	47,0

We did not succeed in preparing the dimethyl ester by the action of sodium dimethyl phosphite. The resulting ester, as was shown in the case of the diethyl ester, readily combines with a molecular proportion of bromine. Attempts to eliminate hydrogen bromide from the dibromide by the action of alcoholic alkali so as to obtain a cyclopentadienylphosphonic ester were not successful because resinification occurred. 2-Cyclopenten-1-ylphosphonic esters are readily oxidized with peroxyacetic acid with formation of the corresponding epoxides. The constants of the compounds obtained are given in Table 2.

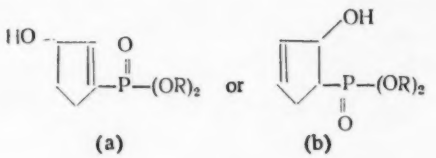
TABLE 2

R = 	B.p. in °C (p in mm)	n_D^{20}	d_0^{20}	MR found	MR calculated*	Yield %
Diethyl	115—115,5 (1)	1,4566	1,1528	52,00	52,57	54,9
Dipropyl	129—130 (2)	1,4555	1,0922	61,74	61,81	77,0
Diisopropyl	126—126,5 (2)	1,4494	1,0861	61,37	61,81	78,0
Dibutyl	145,5—146 (2)	1,4562	1,0660	70,50	71,04	73,0
Diisobutyl	140—141 (1,5)	1,4535	1,0595	70,56	71,04	50,0

* The exaltation of the epoxide ring is taken as 0.7.

In the oxidation of dibutyl and diisobutyl 2-cyclopenten-1-ylphosphonates with peroxyacetic acid, as well as the epoxides we isolated higher-boiling fractions with the following constants: for the dibutyl ester – b. p. 179-180° (2 mm), $n^{20}D$ 1.4864, and d^{20}_4 1.0634 (Found MR 72.30. $C_{13}H_{25}PO_4F$. Calculated MR 71.96); for the diisobutyl ester – b. p. 174-175° (1 mm), $n^{20}D$ 1.4651, and d^{20}_0 1.0555 (Found MR 72.39; $C_{13}H_{25}PO_4F$. Calculated MR 71.96). Both in analysis and in molecular refraction the products corresponded to substances formed by the elimination of one molecule of water from the diols obtained by the hydration of the epoxides. The presence of a double bond in the products was shown by titration with peroxyphthalic acid and by the infrared spectrum of the diisobutyl ester. The spectrum contained an absorption band at 1238 cm^{-1}, corresponding to the P=O group, and a C=C band at 1609 cm^{-1}. An intense band found in the spectrum at 1044 cm^{-1} may be attributable to the hydroxy group of an α,β-unsaturated secondary alcohol [2].

To the products isolated we may tentatively give the following structure:



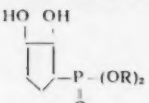
(a) (b)

Formula (a) is supported by the difficulty with which the double bond can be oxidized. The double-bond band in the infrared spectrum, 1609 cm^{-1}, is close to the band of the double bond in unsubstituted cyclopentene (1611 cm^{-1}) [3], which is more in accord with Formula (b). The question of the position of the double bond requires further elucidation. As regards the ways in which these products are formed, it may be suggested that water is eliminated from the corresponding diols, which are formed by the hydration of the epoxides. However, against this view we have the stability of the products of the hydration of the epoxides to vacuum distillation, as will be shown below. It is more probable that hydroxycyclopentenylphosphonic esters are formed by the elimination of acetic acid during distillation from the product of the addition of acetic acid to the epoxide formed in the process of oxidation with peroxyacetic acid.

Attempts to isomerize diethyl epoxycyclopentylphosphonate by heating it in presence of zinc bromide were not successful. The epoxide was recovered unchanged. The stability of the epoxides of the carbocyclic series containing a COOR or CN group in a six-membered ring toward isomerizing agents has been observed previously [4].

The epoxides cited in Table 2 are readily hydrated in aqueous-dioxane solution in presence of hydrochloric acid. The resulting 2,3-dihydroxy-trans-cyclopentylphosphonic esters are viscous liquids, which vacuum-distill without decomposition. Their constants are given in Table 3.

TABLE 3

R = 	B.p. in °C (p in mm)	n_D^{20}	d_0^{20}	MR found	MR calculated	Yield %
Dipropyl	167—169 (1,5)	1,4691	1,1494	64,54	64,71	72
Diisopropyl	148—150 (1,5)	1,4640	1,1427	64,31	64,71	30*
Dibutyl	177—178 (2,0)	1,4627	1,0889	74,41	73,95	31*
Diisobutyl	182—184 (1,0)	1,4654	1,1092	73,42	73,95	36*

* The low yields are to be explained by the small amounts of substances taken for reaction.

EXPERIMENTAL

Reaction of 3-Chlorocyclopentene with Triethyl Phosphite. Triethyl phosphite (21 g) was added to 13 g of 3-chlorocyclopentene [b. p. 18-20° (5 mm); $n^{26}D$ 1.4725 [5]]. No reaction was observed. The bath was heated to 120°, and ethyl chloride began to be liberated and cyclopentadiene distilled off. We obtained 8.5 g of cyclopentadiene, b. p. 30-40° and $n^{18.6}D$ 1.4538. On its reaction with maleic anhydride we obtained the adduct, m. p. 163-165°, undepressed by admixture of the adduct obtained from cyclopentadiene and maleic anhydride. The residue remaining in the flask after the removal of cyclopentadiene was distilled. We obtained 13 g of diethyl hydrogen phosphite; b. p. 56-58° (1.5 mm); $n^{20}D$ 1.4093, d^{20}_0 1.0711.

Reaction of 3-Chlorocyclopentene with Sodium Diethyl Phosphite. Addition was made of 19.5 g (3.5 g excess) of 3-chlorocyclopentene to a solution of 24.9 g of sodium diethyl phosphite in ether. The mixture was refluxed for three hours. Sodium chloride (8 g) was separated by centrifugation. After removal of ether and distillation we obtained 23 g (74%) of diethyl 2-cyclopenten-1-ylphosphonate; b. p. 100-100.5° (3 mm); $n^{20}D$ 1.4579, d^{20}_0 1.0726; found MR 51.94. $C_9H_{17}O_3P_F$. Calculated MR 51.96. Found %: P 15.32. Calculated %: P 15.18. On hydrolysis of the ester with dilute hydrochloric acid we obtained the acid in the form of a noncrystallizing viscous liquid.

For the addition of bromine to the ester, 5.1 g of bromine was added dropwise to 6.5 g of the ester in 25 ml of carbon tetrachloride. Some heat was evolved, and the bromine color disappeared. The carbon tetrachloride was vacuum-distilled off, leaving a pale-yellow liquid.

Reaction of Diethyl 2,3-Dibromocyclopentylphosphonate with Alcoholic Potassium Hydroxide. A solution of 3.5 g of potassium hydroxide in 40 ml of absolute alcohol was added carefully to 11.5 g of the dibromo ester prepared in the previous experiment. Some heat was evolved, and potassium bromide was precipitated. The mixture was heated on a water bath for 30 minutes, the precipitate (6 g) was filtered off, and alcohol was distilled off. The residue was a dark-colored viscous liquid, which could not be vacuum-distilled. A similar picture was obtained when the reaction product was treated with water and extracted with ether. The elimination of hydrogen bromide under the action of alcoholic potassium hydroxide goes at room temperature, but in this case also the reaction product cannot be vacuum-distilled.

Reaction of 3-Chlorocyclopentene with Sodium Dipropyl Phosphite. Sodium (6.7 g) was added to 49 g of dipropyl hydrogen phosphite in 400 ml of dry ether. 3-Chlorocyclopentene (35 g) was added to the resulting solution of sodium dipropyl phosphite. The mixture was refluxed for 20 hours, and a few drops of acetic acid were then added. After the removal of ether the residue was vacuum-distilled (straight from the precipitate).

We then obtained 25.8 g (38.5%) of dipropyl 2-cyclopenten-1-ylphosphonate; b. p. 110-110.5° (1.5 mm); $n^{20}D$ 1.4553, d^{20}_0 1.0235; found MR 60.21. $C_{11}H_{21}PO_3F$. Calculated MR 61.20. Found %: P 13.38. Calculated %: P 13.35.

Reaction of 3-Chlorocyclopentene with Sodium Diisopropyl Phosphite. The procedure was quite analogous to that of the preceding experiment. For reaction we took 47.7 g of sodium diisopropyl phosphite and 26 g of 3-chlorocyclopentene. Distillation gave 15 g (31%) of diisopropyl 2-cyclopenten-1-ylphosphonate; b. p. 96-96.5° (2 mm); $n^{20}D$ 1.4483; d^{20}_0 1.0176; found MR 59.75. $C_{11}H_{21}PO_3F$. Calculated MR 61.20. Found %: P 13.54. Calculated %: P 13.35.

Reaction of 3-Chlorocyclopentene with Sodium Dibutyl Phosphite. As a result of the reaction between 109 g of sodium dibutyl phosphite and 52 g of 3-chlorocyclopentene we isolated 38 g (30%) of dibutyl 2-cyclopenten-1-ylphosphonate; b. p. 122-123° (1 mm); $n^{20}D$ 1.4544, d^{20}_0 1.0053; found MR 70.18. $C_{13}H_{25}PO_3F$. Calculated MR 70.43. Found %: P 12.03. Calculated %: P 11.91.

Reaction of 3-Chlorocyclopentene with Sodium Diisobutyl Phosphite. In the reaction between 58 g of sodium diisobutyl phosphite and 29.5 g of 3-chlorocyclopentene we isolated 34.8 g (47%) of diisobutyl 2-cyclopenten-1-ylphosphonate; b. p. 126.5-127° (4 mm); $n^{20}D$ 1.4531; d^{20}_0 0.9990; found MR 70.45. $C_{13}H_{25}PO_3F$. Calculated MR 70.43. Found %: P 12.10. Calculated %: P 11.91.

Oxidation of Diethyl 2-Cyclopenten-1-ylphosphonate with Peroxyacetic Acid. A solution of 34.6 g of diethyl 2-cyclopenten-1-ylphosphonate in 50 ml of dry ether was prepared in a small flask fitted with reflux condenser, and addition was made of 66.5 ml (10% excess) of a solution of peroxyacetic acid, 1 ml of which contained 0.04474 g of active oxygen. After three days the reaction mixture was neutralized to litmus with 8% potassium hydroxide solution, then extracted with ether and left over fused potassium carbonate overnight. The residue remaining after distillation of ether was vacuum-distilled. This gave 20.5 g (54.9%) of diethyl epoxycyclopentylphosphonate; b. p. 115-115.5° (1 mm); $n^{20}D$ 1.4566; d^{20}_0 1.1528; found MR 52.00. $C_9H_{17}PO_4$. Calculated MR 52.57. Found %: P 14.08. Calculated %: P 14.08.

Attempts to isomerize the epoxide by heating it in dry benzene in presence of fused zinc bromide or by heating it in presence of zinc bromide in sealed tubes at 140° were not successful. The greater part of the epoxide was recovered unchanged. Part of it was resinified.

Oxidation of Dipropyl 2-Cyclopenten-1-ylphosphonate with Peroxyacetic Acid. To a solution of 14.5 g of dipropyl 2-cyclopenten-1-ylphosphonate in 40 ml of dry ether we added 48 ml (twofold excess) of an ethereal solution of peroxyacetic acid, 1 ml of which contained 0.04989 g of active oxygen. After three days the reaction mixture was treated in the usual way. Distillation gave 12 g (77%) of dipropyl epoxycyclopentylphosphonate; b. p. 129-130° (2 mm); $n^{20}D$ 1.4555; d^{20}_0 1.0922; found MR 61.74. $C_{11}H_{21}PO_4$. Calculated MR 61.81. Found %: P 12.41. Calculated %: P 12.49.

Oxidation of Diisopropyl 2-Cyclopenten-1-ylphosphonate with Peroxyacetic Acid. By the oxidation of 11.5 g of diisopropyl 2-cyclopenten-1-ylphosphonate with 34 ml (twofold excess) of the same solution of peroxyacetic acid we obtained 9.5 g (78%) of diisopropyl epoxycyclopentylphosphonate; b. p. 126-126.5° (2 mm); $n^{20}D$ 1.4494; d^{20}_0 1.0861; found MR 61.37. $C_{11}H_{21}PO_4$. Calculated MR 61.81. Found %: P 12.47. Calculated %: P 12.49.

Oxidation of Dibutyl 2-Cyclopenten-1-ylphosphonate with Peroxyacetic Acid. On oxidation with the same solution of peroxyacetic acid (72 ml, twofold excess), 26 g of dibutyl 2-cyclopenten-1-ylphosphonate gave 19 g (73%) of dibutyl epoxycyclopentylphosphonate; b. p. 179-180° (2 mm); $n^{20}D$ 1.4562; d^{20}_0 1.0660; found MR 70.50. $C_{13}H_{25}PO_4$. Calculated MR 71.04. Found %: P 11.53. Calculated %: P 11.22.

In addition we isolated 2.5 g (9%) of a higher-boiling fraction; b. p. 179-180° (2 mm); $n^{20}D$ 1.4684; d^{20}_0 1.0634; found MR 72.30. $C_{13}H_{25}PO_4F$. Calculated MR 71.96. Found %: P 11.43. Calculated %: P 11.22.

Oxidation of Diisobutyl 2-Cyclopenten-1-ylphosphonate with Peroxyacetic Acid. On oxidation with the same solution of peroxyacetic acid (83 ml, twofold excess), 26.7 g of the ester gave 13.7 g (50%) of diisobutyl epoxycyclopentylphosphonate; b. p. 140-141° (1.5 mm); $n^{20}D$ 1.4535; d^{20}_0 1.0595; found MR 70.56. $C_{13}H_{25}PO_4$. Calculated MR 71.04. Found %: P 11.20; mol. wt. (Rast's method) 272.5; Calculated %: P 11.22; mol. wt. 276.35.

In addition we isolated 3.7 g (14%) of a higher-boiling fraction; b. p. 174-175° (1 mm); $n^{20}D$ 1.4651; d^{20}_0 1.0555; found MR 72.39; mol. wt. (Rast's method) 291.6. $C_{13}H_{25}PO_4F$. Calculated MR 71.96; mol. wt. 276.35.

The high molecular weight may be explained by the association of the substance. The substance was oxidized with a solution of peroxyphthalic acid, 1 ml of which contained 0.04744 g of active oxygen. Titration with sodium thiosulfate solution after one day showed that the double bond was oxidized to the extent of 33.37%; after four days the figure was 43.64%, and after 13 days it was 56.47%.

Hydration of Diisobutyl Epoxycyclopentylphosphonate. To a solution of 4.5 g of the substance in 10 ml of dioxane in a small Arbuzov flask we added 3 ml of water (tenfold excess) and 0.5 ml of concentrated hydrochloric acid. On the next day water and dioxane were vacuum-distilled off, and the residue was vacuum-distilled. We isolated 1.7 g (36%) of dibutyl 2,3-dihydroxycyclopentylphosphonate; b. p. 182-184° (1 mm); $n^{20}D$ 1.4654; d^{20}_0 1.1092; found MR 73.42. $C_{13}H_{27}PO_5$. Calculated MR 73.95. Found %: P 10.85. $C_{13}H_{27}PO_5$. Calculated %: P 10.53.

Hydration of Dibutyl Epoxycyclopentylphosphonate. Water (3 ml) and hydrochloric acid (0.5 ml) were added to a solution of 4 g of the substance in 10 ml of dioxane in a small Arbuzov flask. On the next day water and dioxane were distilled off, and vacuum distillation of the residue gave 1.3 g (31%) of dibutyl 2,3-dihydroxycyclopentylphosphonate; b. p. 177-178° (2 mm); $n^{20}D$ 1.4627; d^{20}_0 1.0889; found MR 74.41. $C_{13}H_{27}PO_5$. Calculated MR 73.95. Found %: P 10.57. $C_{13}H_{27}PO_5$. Calculated %: P 10.53.

Hydration of Dipropyl Epoxycyclopentylphosphonate. Water (2.5 ml) and hydrochloric acid (0.5 ml) were added to a solution of 2.7 g of the substance in 10 ml of dioxane in a small Arbuzov flask. On the next day, after removal of water and dioxane, we isolated 1.8 g (72%) of dipropyl 2,3-dihydroxycyclopentylphosphonate; b. p. 167-169° (1.5 mm); $n^{20}D$ 1.4691; d^{20}_0 1.1494; found MR 64.54. $C_{11}H_{23}PO_5$. Calculated MR 64.71. Found %: P 11.62. Calculated %: P 11.64.

Hydration of Diisopropyl Epoxycyclopentylphosphonate. The hydration was carried out as in the preceding experiment. From 2.5 g of diisopropyl epoxycyclopentylphosphonate we isolated 0.8 g (30%) of diisopropyl 2,3-dihydroxycyclopentylphosphonate; b. p. 148-150° (1.5 mm); $n^{20}D$ 1.4640; d^{20}_0 1.1427; found MR 64.31. $C_{11}H_{23}PO_5$. Calculated MR 64.71. Found %: P 11.80. Calculated %: P 11.64.

SUMMARY

1. By the action of sodium dialkyl phosphites on 3-chlorocyclopentene, 2-cyclopenten-1-ylphosphonic esters were synthesized.

2. By the oxidation of the resulting esters with peroxyacetic acid the corresponding epoxides were prepared. Hydration of the esters gave trans-2,3-dihydroxycyclopentylphosphonic esters.*

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TAUTOMERISM AND GEOMETRIC ISOMERISM OF NITROGEN CONTAINING DERIVATIVES OF CARBONYL COMPOUNDS

COMMUNICATION 2. POLAROGRAPHIC STUDY OF THE TRANSFORMATIONS OF PHENYLHYDRAZONES OF SOME ALDEHYDES AND ALIPHATIC-AROMATIC KETONES IN METHANOL

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Original article submitted March 20, 1959

In the preceding communication [1] we described the transformations of the phenylhydrazones of acetone, butanone, 3-methyl-2-butanone, and cyclohexanone and of the ethylphenylhydrazone of acetone occurring on their dissolution in methanol. By the use of the polarographic method, we showed that phenylhydrazones of aliphatic ketones are in general capable of existing in three tautomeric forms and for each of these syn and anti isomers are possible. On dissolution in alcohol, tautomeric equilibrium moves in the direction of the azo form (III).

$$\underset{\text{(I)}}{C_6H_5NHNH{-}\overset{\displaystyle R}{\overset{|}{C}}{=}CHR'} \rightleftharpoons \underset{\text{(II)}}{C_6H_5NH{-}N{=}\overset{\displaystyle R}{\overset{|}{C}}{-}CH_2R'} \rightleftharpoons \underset{\text{(III)}}{C_6H_5N{=}N{-}\overset{\displaystyle R}{\overset{|}{C}}H{-}CH_2R'}$$

It was found that in the free state the phenylhydrazones of the ketones studied have the structure of the ene-hydrazine type (I). Having determined the potentials of the half-waves of the tautomers and stereoisomers, we calculated the energies of their mutual transitions. It was of interest to continue this investigation, extending it to phenylhydrazones of other carbonyl compounds with the object of determining the effect of structure on tautomeric transformations. As a result of such an investigation, we hoped to find an explanation for the difference in the tendency to ring-close into heterocycles in the Fischer reaction in different phenylhydrazones. In the present communication, we describe the behavior, on dissolution in methanol, of the phenylhydrazones of acetophenone, 4'-chloroacetophenone, acetaldehyde, isobutyraldehyde, and benzaldehyde, studied with the aid of polarography by the previously described method.

In Figs. 1-4 are shown families of polarograms (6-7 curves each) obtained during the keeping of solutions, and in Table 1 their numerical characteristics are given. The polarograms of a solution of benzaldehyde phenylhydrazone, which we used in the interpretation of the curves, are given in the preceding communication [1]. Unlike the polarograms of the phenylhydrazones of aliphatic and alicyclic ketones, the initial polarograms of the compounds now described had a fundamental wave at a less negative potential than -1.4 v. However, during the keeping of solutions of the phenylhydrazones of acetophenone, 4'-chloroacetophenone, and benzaldehyde there was noted the appearance, and increase in intensity with time of waves of more negative potentials than those of the initial waves. In these cases the solutions simultaneously acquired the characteristic odor of either acetophenone, 4'-chloroacetophenone, or benzaldehyde, and these compounds are reduced under our

conditions at the very potentials at which these waves appear, and we established, therefore, that these phenylhydrazones hydrolyzed with accumulation of the carbonyl compounds in the solution. It is true that we were not altogether clear how such hydrolysis occurred in methanol solution. There appeared to be reaction of the

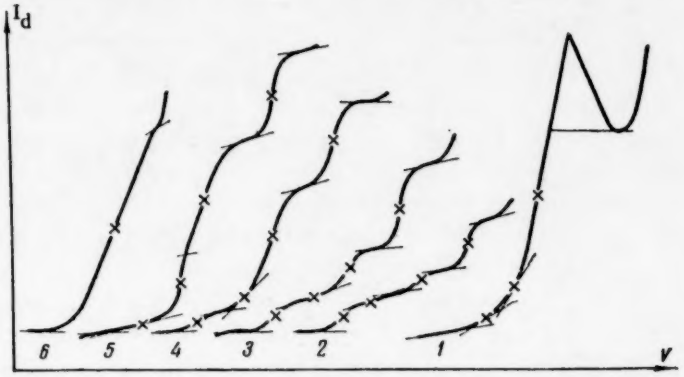


Fig. 1. Polarograms of acetophenone phenylhydrazone.

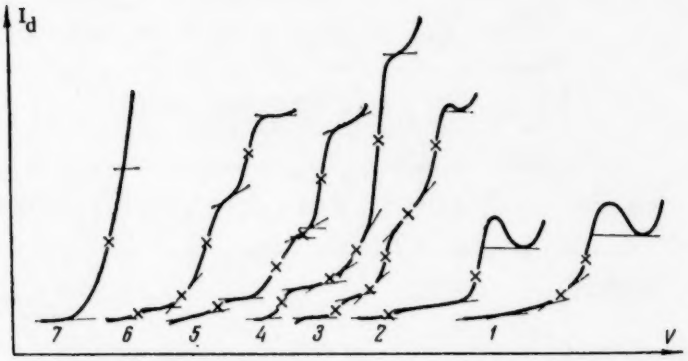
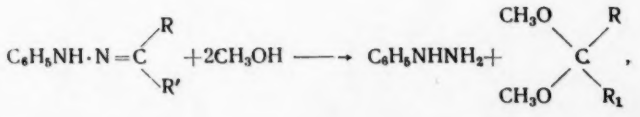


Fig. 2. Polarograms of 4'-chloroacetophenone phenylhydrazone.

hydrazone with alcohol leading to the formation of compounds that were readily decomposed by the water of the electrolyte with formation of carbonyl compounds. It is most likely that ketals or acetals were first formed by the equation:



and these were hydrolyzed on addition of the alcoholic solution to the borate buffer with formation of acetophenone, 4'-chloroacetophenone, or benzaldehyde, but this hypothesis requires experimental verification. In general, however, with the passage of time the following changes occurred on the polarograms of the solutions studied: the initial waves usually diminished in intensity, and new waves appeared at more negative potentials. These changes were less regular than those described in Communication I [1], but they clearly indicated the appearance of some or other new forms of phenylhydrazones in the solutions. The absence of regularity in changes

TABLE 1

Compound	Polarogram No.	Time of keeping soln. (hr)	Wave characteristics											
			I		II		III		IV		V		VI	
			$E_{1/2}$ (V)	H (mm)	$E_{1/2}$ (V)	H (mm)	$E_{1/2}$ (V)	H (mm)	$E_{1/2}$ (V)	H (mm)	$E_{1/2}$ (V)	H (mm)	$E_{1/2}$ (V)	H (mm)
Acetophenone	1	0	—	—	—	—	1,15	52	1,02	15	0,80	9	—	—
	2	49	1,61	18	—	—	1,27	8	—	—	0,92	4	0,72	10
	3	95	1,61	30	—	—	1,28	13	—	—	0,99	8	0,68	10
	4	320	1,61	31	—	—	1,18	34	—	—	0,98	11	0,64	6
	5	870	1,61	31	—	—	1,12	42	—	—	0,94	21	0,68	7
Acetophenone	6	—	1,62	75	—	—	—	—	—	—	—	—	—	—
4'-Chloroacetophenone phenylhydrazone	1	0	—	—	—	—	1,27	21	—	—	0,88	10	—	—
	2	3	—	—	—	—	1,27	24	—	—	—	—	0,62	4
	3	45	1,48	36	—	—	1,27	18	1,06	22	0,92	17	0,64	9
	4	70	1,51	77	—	—	1,30	23	1,12	6	—	—	0,62	13
	5	211	1,50	88	—	—	1,36	8	1,09	56	—	—	0,57	10
	6	550	1,52	72	—	—	1,36	8	1,13	72	0,91	22	0,56	10
4'-Chloroacetophenone	7	—	1,51	67	—	—	—	—	—	—	—	—	—	—
Acetaldehyde phenylhydrazone	1	0	—	—	1,33	17	1,13	5	—	—	—	—	—	—
	2	0,5	—	—	1,36	27	1,15	19	—	—	—	—	—	—
	3	2,5	—	—	1,35	16	—	—	1,07	15	—	—	—	—
	4	8	—	—	1,35	18	—	—	1,07	7	0,89	3	—	—
	5	48,5	—	—	1,33	33	—	—	1,05	11	0,70	11	—	—
	6	97	—	—	1,34	5	—	—	1,02	2	0,78	10	0,56	67
	7	148	—	—	1,32	8	—	—	1,06	3	0,86	4	0,50	50
Isobutylraldehyde phenylhydrazone	1	0	—	—	1,31	29	—	—	—	—	0,89	7	—	—
	2	1	—	—	1,34	31	1,17	8	—	—	0,89	22	—	—
	3	3	—	—	1,37	40	1,25	18	—	—	0,90	37	—	—
	4	21	—	—	1,36	32	1,19	28	—	—	0,90	126	—	—
	5	30	—	—	1,29	40	—	—	1,10	17	0,89	163	—	—
	6	244	—	—	1,32	67	—	—	1,08	24	0,80	116	—	—
Benzaldehyde phenylhydrazone	1	0	—	—	—	—	1,12	59	—	—	—	—	—	—
	2	13	1,33	20	—	—	1,11	62	—	—	0,85	14	0,54	7
	3	20	1,37	34	—	—	1,18	19	0,96	4	—	—	0,58	3
	4	36	1,37	42	—	—	1,20	8	1,04	31	0,89	9	0,56	7
	5	68	1,37	76	—	—	1,20	17	1,08	28	0,89	15	0,56	11
Benzaldehyde	6	—	1,36	82	—	—	—	—	—	—	—	—	—	—

in the character of the curves was probably due to the fact that every time that an alcoholic solution of a phenylhydrazone was added to the borate buffer serving as ground solution transformations due to the dilution and change of the medium occurred.

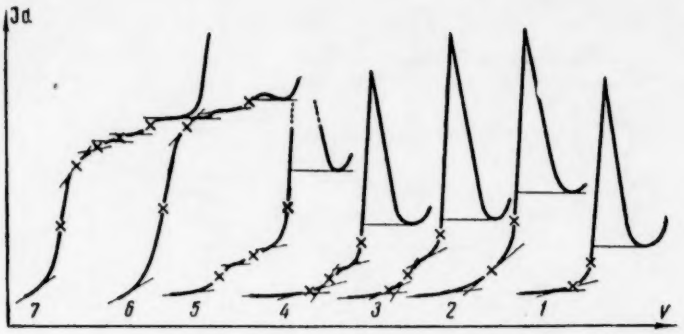


Fig. 3. Polarograms of acetaldehyde phenylhydrazone.

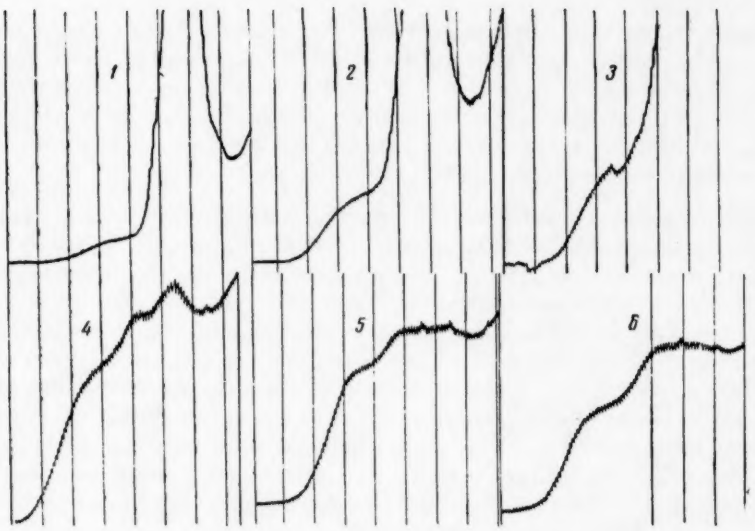


Fig. 4. Polarograms of isobutyraldehyde phenylhydrazone.

Hence, with the method adopted the state of the substance in the solution was not correctly portrayed on the polarograms. At this stage this was not a serious obstacle because we were primarily interested in the question of whether ene-hydrazine forms of arylhydrazines exist. In the future, we propose to study the kinetics of the transformations and the positions of equilibrium in various media by the use of another method.

The families of polarograms obtained from solutions of the phenylhydrazones of acetophenone, 4'-chloroacetophenone, acetaldehyde, and isobutyraldehyde were interpreted in the way described previously [1]. In Table 2 we give the values found in this way for the potentials of half-waves of tautomers and stereoisomers and the energies of their mutual transitions. The interpretation of the polarograms showed that in freshly prepared solution, and probably in the free state, the phenylhydrazones of acetophenone, 4'-chloroacetophenone, and benzaldehyde have the hydrazone structure. The phenylhydrazones of acetaldehyde and isobutyraldehyde also appear to have the hydrazone structure in the free state, but on dissolution in alcohol pass into the ene-hydrazines,

which in solution are in equilibrium with the other tautomeric forms. The correctness of this view is supported by the fact that the wave of the ene-hydrazine forms of these compounds not only did not disappear with time, but even increased in height for a considerable time, i.e., the formation of this form occurred in the solution.

TABLE 2

Phenylhydrazone of	Azo form				Hydrazone form				Ene-hydrazine form	
	$E_{\frac{1}{2}}$ of the isomers (v)		transition energy (kcal/mole)		$E_{\frac{1}{2}}$ of the isomers (v)		transition energy (kcal/mole)		$E_{\frac{1}{2}}$ of the isomers (v)	
	syn	anti	syn→anti	hydrazone→azo cpd.	syn	anti	syn→anti	*	syn	anti
Acetophenone	0,65	0,98	15,2	18,4	1,15	1,28	6,0	—	—	—
4'-Chloroacetophenone	0,64	0,92	12,9	17,0	1,06	1,27	9,7	—	—	—
Acetaldehyde	0,50	0,78	12,9	19,3	1,05	1,15	5,0	11,5	1,35	
Isobutyraldehyde		0,89		11,3	1,08	1,19	5,4	10,8	1,37	
Benzaldehyde	0,56	0,89	15,2	18,9	1,08	1,20	5,5	—	—	—

*ene-hydrazine→hydrazone.

The results obtained in the present work do not permit us to assert that under the conditions described the phenylhydrazones of acetophenone and 4' chloroacetophenone do not form ene-hydrazines, because the ketones arising by hydrolysis (or alcoholysis) were reduced at potentials very close to those for the reduction of the ene-hydrazine forms of their phenylhydrazones. The above-noted hydrolysis (alcoholysis) appeared to occur only in those cases in which a large amount of the hydrazone form was kept in the solution for a long time, which is in accord with the above-suggested reaction scheme.

We consider that the polarographic data on the structure of phenylhydrazones are in accord with the observations of Grammaticakis [2-5] on the reactions of phenylhydrazones with mixed organomagnesium compounds and enable us to give these an explanation. Phenylhydrazones of aldehydes of hydrazone structure in ether solution undergo addition with a Grignard reagent because these contain an azomethine group, whereas phenylhydrazones of ketones which have an ene-hydrazine structure do not contain this group and do not combine with a Grignard reagent. Cyclohexanone phenylhydrazone, as shown in [1], rapidly forms the hydrazone and azo forms on dissolution, which makes them capable of reacting with organomagnesium compounds. The behavior in Grammaticakis's reaction of the phenylhydrazones of aliphatic-aromatic ketones which do not combine with a Grignard reagent does not conflict with the view of their hydrazone structure, because the behavior may be due to interaction between the double bond of the azomethine group and bonds of the aromatic ring of the ketone. Our results show also that the double bond of the azomethine group is extremely mobile, which in our opinion is the main cause of the lowering of the "rigidity" [6] of this bond.

EXPERIMENTAL

The phenylhydrazones required in the work were prepared by the usual methods, as recommended in the literature. In Table 3 we give the characteristics of the hydrazones used in the present work.

The apparatus and polarography conditions are described in the preceding communication [1]. Isobutyraldehyde phenylhydrazone was studied under the same conditions, but on a Heyrovsky LP-55 photorecording polarograph with a galvanometer of sensitivity $3.1 \cdot 10^{-9}$ amp for 1 mm of the scale.

The solutions for study contained the following in 50 ml of methanol: acetophenone phenylhydrazone 0.1208 g, 4'-chloroacetophenone phenylhydrazone 0.0469 g, acetaldehyde phenylhydrazone 0.0591 g, and isobutyraldehyde phenylhydrazone 0.1053 g.

For the determination of the polarograms of the phenylhydrazones of acetophenone and 4'-chloroacetophenone we took, per 10 ml of ground solution, 0.3 ml of the alcoholic solution of the first and 1.0 ml of the

alcoholic solution of the second. With these proportions of components the contents of the polarographic cell were at first turbid, but after a certain time the alcoholic solutions already gave a clear electrolyte in the cell, i.e., the transformations occurring in the alcoholic solutions of these compounds were accompanied by a change in solubility.

TABLE 3

Phenylhydrazone of	M.p. (°C)	B.p. in °C (p in mm)	n_D^{20}	Yield (%)
Acetophenone	104,5	—	—	98
4'-Chloroacetophenone	113—114	—	—	94
Acetaldehyde	93—95	—	—	—
Isobutyraldehyde	—	132(10)	1,5684	81

The polarography of acetophenone phenylhydrazone was carried out at $^1/_{50}$ of the maximum sensitivity of the galvanometer, and that of 4'-chloroacetophenone phenylhydrazone at $^1/_{10}$ (Curve 5 was taken at $^1/_{25}$). In the study of the solution of acetaldehyde phenylhydrazone we took 2.0 ml for 10 ml of ground solution and worked at $^1/_{25}$ of the sensitivity of the galvanometer. The proportions of the components of the electrolyte were the same also for the polarography of isobutyraldehyde phenylhydrazone, the data for which are given for $^1/_{30}$ of the maximum sensitivity of the galvanometer.

SUMMARY

1. With the aid of polarography a study was made of the tautomeric and stereoisomeric transformations of the phenylhydrazones of acetophenone, 4'-chloroacetophenone, acetaldehyde, and isobutyraldehyde in alcoholic solutions.

2. In a freshly prepared solution the phenylhydrazones of acetophenone, 4'-chloroacetophenone, and benzaldehyde have hydrazone structures, which appear to be their structures in the free state. In the free state the phenylhydrazones of acetaldehyde and isobutyraldehyde probably also have the hydrazone structure, but on dissolution in alcohol they pass into the ene-hydrazine structure, which is probably in equilibrium with the other tautomeric forms.

3. The potentials of the half-waves of the tautomers and stereoisomers of the compounds studied were determined, and from these the energies of mutual transitions were calculated.

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REACTIONS OF FLUORO OLEFINS

COMMUNICATION 13. CATALYTIC HYDROGENATION OF PERFLUORO OLEFINS

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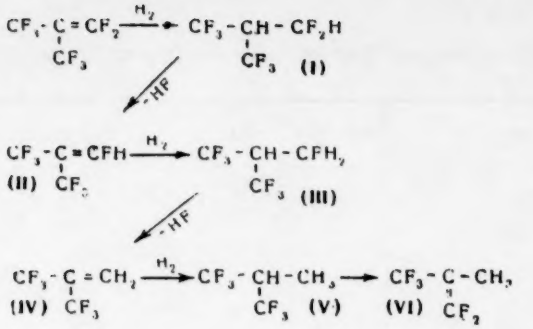
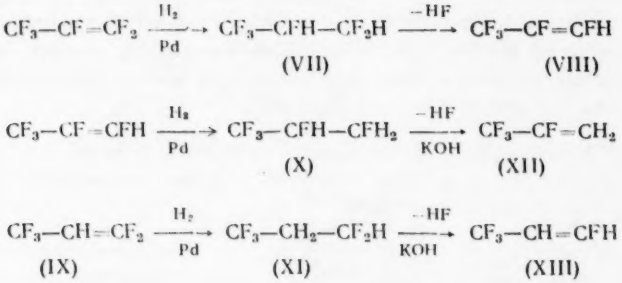
Apart from its practical importance, the study of the catalytic hydrogenation of perfluoro olefins has a direct bearing on the theory of heterogeneous catalysis. As the rate of hydrogenation must be directly related to the state of the π-bond of the olefins and increase with reduction in its electron density, it may be supposed that the hydrogenation of perfluoro olefins, which have a strong affinity for nucleophiles, will proceed very readily and that in the series of perfluoro olefins the ease of hydrogenation will increase from perfluoroethylene to perfluoroisobutene; this view corresponds to the observations of Schuster [1] on the diminution in the rate of hydrogenation of the usual olefins as we pass from ethylene through propene to isobutene, and also to the results of Park's work [2] on the comparison of the heats of hydrogenation of vinyl chloride and chlorotrifluoroethylene. Our work on the hydrogenation of perfluoroethylene, perfluoropropene, and perfluoroisobutene showed that perfluoro olefins are hydrogenated smoothly with molecular hydrogen over palladium and nickel catalysts [3, 4]. Over a palladium catalyst (1% Pd/Al_2O_3) at room temperature products of the normal addition of hydrogen are formed almost exclusively in quantitative yield: 1,1,2,2-tetrafluoroethane, 1,1,1,2,3,3-hexafluoropropane, and 2-(difluoromethyl)-1,1,1,3,3,3-hexafluoropropane, respectively. Hydrogenation over a nickel catalyst (reduced nickel oxide) requires a higher temperature (60-100°) and leads to a mixture of hydrogenation products, consisting of the normal products and products of the replacement of fluorine by hydrogen, e.g., 1,1,2-trifluoroethane, in the hydrogenation of perfluoroethylene, and 1,1,1,3,3,3-hexafluoro-2-methylpropane, in the hydrogenation of perfluoroisobutene. In the hydrogenation of chlorotrifluoroethylene over 1% Pd/Al_2O_3 at room temperature replacement of chlorine by hydrogen occurred with the formation of trifluoroethylene and its subsequent hydrogenation. Under certain experimental conditions $CF_2=CFH$ is the main reaction product and can be obtained in about 60% yield together with trifluoroethane.

The hydrogenation of perfluorobutadiene proceeded with the formation of 1,1,2,3,4,4-hexafluorobutane. The dehydrofluorination of fluoro hydrocarbons obtained by the hydrogenation of perfluoro olefins made it possible to prepare some previously unknown or difficultly accessible fluoro olefins. Thus, the product of the hydrogenation of perfluoroisobutene, 2-(difluoromethyl)-1,1,1,3,3,3-hexafluoropropane (I), readily eliminates hydrogen fluoride, even under the action of aqueous alkali, with formation of 1,3,3,3-tetrafluoro-2-(trifluoromethyl)propene (II). The structure of the olefin obtained was proved by its oxidation to hexafluoroacetone, which simultaneously confirmed the structure of the original 2-(difluoromethyl)-1,1,1,3,3,3-hexafluoropropane, to which a different boiling point had previously been attributed [5]. Further hydrogenation of 1,3,3,3-tetrafluoro-2-(trifluoromethyl)propene gave 1,1,1,3,3,3-hexafluoro-2-(fluoromethyl)propane (III), the dehydrofluorination of which readily gave the previously difficultly accessible 3,3,3-trifluoro-2-(trifluoromethyl)propene (IV) [6].

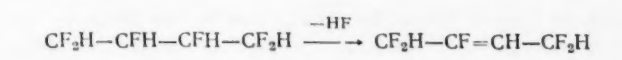
3,3,3-Trifluoro-2-(trifluoromethyl)propene (IV) was hydrogenated over a palladium catalyst with formation of 1,1,1,3,3,3-hexafluoro-2-methylpropane (V); the latter, as indicated above, was obtained in considerable amount in the hydrogenation of perfluoroisobutene over a nickel catalyst at about 100°. The dehydrofluorination



of this fluoro hydrocarbon with the formation of 1,1,3,3,3-pentafluoro-2-methylpropene (VI) occurred when it was passed through a melt of 90% potassium hydroxide at 170°. The hydrogenation product from perfluoropropene, 1,1,1,2,3,3-hexafluoropropane (VII), was readily dehydrofluorinated with formation of 1,2,3,3,3-pentafluoropropene (VIII), which is isomeric with the known 1,1,3,3,3-pentafluoropropene (IX) [7]. The structure of the olefin obtained was proved by a comparison of the nuclear magnetic resonance spectra of these olefins and by their further transformations on hydrogenation and dehydrogenation. Thus, on the hydrogenation of 1,2,3,3,3-pentafluoropropene we obtained 1,1,1,2,3-pentafluoropropane (X), b. p. 20°, the nuclear magnetic spectrum of which differed greatly from that of 1,1,1,3,3-pentafluoropropane (XI), b. p. 12°, obtained by the hydrogenation of 1,1,3,3,3 pentafluoropropene. By the dehydrofluorination of these hydrogenation products we obtained, respectively, the olefins 2,3,3,3-tetrafluoropropene (XII), b. p. − 28° [7], and 1,3,3,3-tetrafluoropropene (XIII), b. p. − 16° [8, 9].



In the hydrogenation of 1,2,3,3,3-pentafluoropropene, together with the main reaction product 1,1,1,2,3-pentafluoropropane, we isolated 1,1,1,2-tetrafluoropropane $CF_3-CFH-CH_3$, b. p. − 1°. The dehydrofluorination of the hydrogenation product from perfluorobutadiene, 1,1,2,3,4,4-hexafluorobutane, occurred with the elimination of one molecule of HF from the 2,3-positions:



The structure of the resulting olefin was proved by its oxidation to difluoroacetic acid.

The study of the catalytic hydrogenation of perfluoro olefins widens the possibilities for the synthesis of saturated and unsaturated fluoro hydrocarbons. The usual general method for the preparation of fluorine-containing compounds is the replacement of hydrogen atoms by halogen and further fluorination. Catalytic hydrogenation with subsequent dehydrofluorination leads to a process of stepwise replacement of fluorine atoms by hydrogen, and in this case the fluorine- and hydrogen containing olefins that cannot be obtained by the usual method become accessible. Moreover, this method makes it possible to prepare compounds in an individual, pure state, which is usually not attained by the halogenation method (see table). The work is being continued, particularly in relation to the kinetics of the hydrogenation of perfluoro olefins.

TABLE

Compounds Obtained by Catalytic Hydrogenation and Dehydrofluorination Reactions

No.	Formula	B.p. (°C)	No.	Formula	B.p. (°C)
1	CF_2H-CF_2H	—22,5	12	$CF_3-C(CF_3)=CFH$	17
2	CF_2H-CFH_2	3	13	$CF_3-CH(CF_3)-CFH_2$	40
3	$CF_2=CFH$	—51	14	$CF_3-C(CF_3)=CH_2$	13
4	$CF_3-CFH-CF_2H$	5	15	$CF_3-CH(CF_3)-CH_3$	21
5	$CF_3-CF=CFH$	—20	16	$CF_3-C(CH_3)=CF_2$	12
6	$CF_3-CFH-CFH_2$	20	17	$CF_2H-CFH-CFH-CF_2H$	65
7	$CF_2=CF-CH_3$	—28	18	$CF_2H-CF=CH-CF_2H$	56
8	$CF_3-CFH-CH_3$	— 1			
9	$CF_3-CH_2-CF_2H$	12			
10	$CF_3-CH=CFH$	—16			
11	$CF_3-CH(CF_3)-CF_2H$	33			

EXPERIMENTAL

Preparation of Palladium Catalyst. Calcined alumina (41 g) in the form of small pieces, 4-5 mm in diameter, was immersed in a solution of 0.87 g of palladium chloride in 100 ml of water and left for several hours. The solution was decanted, and a mixture of 5 ml of 38% formaldehyde solution, 10 ml of 2 N NaOH, and 75 ml of water was added to the residue. After several hours the resulting catalyst was washed with distilled water until alkali was completely removed, placed in the electrically heated reaction tube, and dried in a stream of air at 250-280°. We obtained 39 g of Pd/Al_2O_3 catalyst.

Preparation of Nickel Catalyst. Pieces of compressed nickel oxide, diameter 3-4 mm, were placed in a hydrogenation tube and heated in a stream of hydrogen at 300° until water ceased to be liberated. The resulting nickel catalyst was preserved in a hydrogen atmosphere.

Hydrogenation of Tetrafluoroethylene. 1. Through a glass tube containing nickel catalyst obtained by the reduction of 70 g of nickel oxide we passed 20 liters (STP) of a mixture containing 40% of C_2F_4 and 60% of H_2. The rate of passage was 4.6 liters/hr. At the start of the experiment the temperature rose as a result of the exothermic character of the reaction from 95° to 158°, and it then remained at this level. As a result of the reaction we obtained 28.5 g of condensate, which was collected in a trap at −60°, and distillation of this through a column gave 24.2 g (66%) of tetrafluoroethane, b. p. − 22.5°, and 4.2 g of trifluoroethane, b. p. 2.5°. The total yield was 80% on the tetrafluoroethylene taken. The literature gives: CF_2HCF_2H has b. p. − 23° [10], and CF_2HCFH_2 has b. p. 3° [11].

2. A mixture (35.2 liters at STP) of 40% of C_2F_4 and 60% of H_2 was passed through a glass tube containing 5.6 g of 1% Pd/Al_2O_3 at 5.25 liters/hr. The temperature rose from 19° to 90° and remained in the range 85-90°. In the experiment 63.5 g of substance was condensed, and from this we obtained 62.4 g of tetrafluoroethane by distillation. The condensate did not contain trifluoroethane. The yield of CF_2HCF_2H on the amount of tetrafluoroethylene taken was 97.3%.

Hydrogenation of Chlorotrifluoroethylene. A mixture (18.65 liters at STP) of 40% of chlorotrifluoroethylene (by volume) and 60% of H_2 was passed for three hours at room temperature through a tube containing 15 g of 1% Pd/Al_2O_3. The gaseous reaction products were passed through a vessel containing aqueous NaOH for the absorption of HCl and were condensed in a receiver cooled to − 78°. As a result of the reaction we collected 27.2 g of condensate, from which, after distillation, we obtained 5 g of unchanged chlorotrifluoroethylene, 14 g of trifluoroethylene, b. p. − 51°, and 6.7 g of trifluoroethane, b. p. 3°. The over-all yield of trifluoroethylene and

trifluoroethane was 75.5% on the amount of chlorotrifluoroethylene taken for reaction. The yield of $CF_2=CFH$ was 51%; it was identified as its dibromide $CF_2BrCFHBr$, b. p. 76° and $n^{20}D$ 1.415 [12].

Hydrogenation of Perfluoropropene. A mixture (18 liters at STP) of 40% of perfluoropropene and 60% of H_2 was passed at 3 liters/hr over 15 g of 1% Pd/Al_2O_3. At the start of the experiment the temperature rose from 20° to 50°, and during the hydrogenation it kept at 50°. As a result of the reaction 50.4 g of substance was condensed in the receiver, which was cooled to − 70°; from this distillation gave 48.4 g (96% on perfluoropropene taken) of 1,1,1,2,3,3-hexafluoropropane, b. p. 4-5°. Found %: C 23.33; H 1.28; F 74.53; mol. wt. 151 $C_3H_2F_6$. Calculated %: C 23.67; H 1.31; F 75.00; mol. wt. 152.

Hydrogenation of Perfluoroisobutene. 1. A mixture (18.7 liters at STP) of 40% of perfluoroisobutene (by volume) and 60% of H_2 was passed at 3 liters/hr over 15 g of 1% palladium on alumina. At the start of the experiment the temperature rose from 20° to 60°, and during the hydrogenation it kept at 55-60°. As a result of the reaction 65 g of substance was condensed in the receiver, which was cooled to − 60°; from this distillation through a column gave 8 g of unchanged perfluoroisobutene and 57% (85% on the perfluoroisobutene taken) of 2-(difluoromethyl)-1,1,1,3,3,3-hexafluoropropane, b. p. 33-34° and d^{20}_4 1.558. Found %: C 23.88; H 1.06; F 74.76; mol. wt. 202.8. $C_4H_2F_8$. Calculated %: C 23.76; H 0.99; F 75.25; mol. wt. 202.

2. A mixture (37.2 liters at STP) of 20% of perfluoroisobutene and 80% of H_2 was passed at 100-130° through a glass tube containing nickel catalyst prepared by the reduction of 100 g of nickel oxide. The reaction products were passed through a wash bottle containing aqueous alkali and were condensed in a trap cooled to − 60°. Distillation of 50 g of the mixture of hydrogenation products gave 12 g of unreacted perfluoroisobutene, 5.5 g (10%) of 2-(difluoromethyl)-1,1,1,3,3,3-hexafluoropropane, b.p. 33-34°, and 32.1 g (70% on the perfluoroisobutene that reacted) of 1,1,1,3,3,3-hexafluoro-2-methylpropane, b.p. 21°. Found%: C 28.46; H 2.35; mol. wt. 166. Calculated %: C 28.91; H 2.35; mol. wt. 166. $C_4H_4F_6$. According to the literature [13] 1,1,1,3,3,3-hexafluoro-2-methylpropane has b.p. 21°.

Dehydrofluorination of 2-(Difluoromethyl)-1,1,1,3,3,3-hexafluoropropane. 2-(Difluoromethyl)-1,1,1,3,3,3-hexafluoropropane (50 g) was added gradually to 30% aqueous KOH (40 ml), and the mixture was heated for 15-20 minutes at 40-50° under reflux; the reaction products were then distilled off into a trap cooled to − 70°. We obtained 46 g of condensate, from which by distillation through a column we isolated 7 g of unchanged 2-(difluoromethyl) 1,1,1,3,3,3-hexafluoropropane and 35 g (76%) of 1,3,3,3-tetrafluoro-2-(trifluoromethyl) propene, b. p. 17- 18°. Found %: C 25.96; H 0.64; F 73.17; mol. wt. 182.5. C_4HF_7. Calculated %: C 26.37; H 0.54; F 73.07; mol. wt. 182.

Oxidation of 1,3,3,3-Tetrafluoro-2-(trifluoromethyl)propene. 1,3,3,3-Tetrafluoro-2-(trifluoromethyl) propene (16 g) was gradually added to a stirred solution of 30 g of potassium permanganate in 130-150 ml of water warmed to 35-40°; the reaction mixture was heated further for 2-2.5 hours under reflux at 30-40°. Sulfur dioxide was passed through the cooled solution until colorless, and the precipitate was filtered off and washed with hot water; the filtrate was extracted with ether for 24 hours in a continuous-extraction apparatus. The ether extract was dried with anhydrous magnesium sulfate and distilled. After the removal of ether we obtained 8 g (50%) of hexafluoroacetone hydrate, b. p. 55° (80 mm) and $n^{20}D$ 1.332. The semicarbazone had m. p. 153°, undepressed by admixture of a sample of hexafluoroacetone semicarbazone prepared by the oxidation of perfluoroisobutene [14, 15].

Hydrogenation of 1,3,3,3-Tetrafluoro-2-(trifluoromethyl)propene. A mixture of 40 g of gaseous 1,3,3,3-tetrafluoro-2-(trifluoromethyl)propene and hydrogen (2:3 by volume) was passed over 1% Pd/Al_2O_3 at room temperature. The hydrogenation gave 34 g (80%) of 1,1,1,3,3,3-hexafluoro-2-(fluoromethyl)propane, b. p. 39-40°. Found %: C 26.10; H 1.66; F 72.29. $C_4H_3F_7$. Calculated %: C 26.08; H 1.62; F 72.28.

Dehydrofluorination of 1,1,1,3,3,3-Hexafluoro-2-(fluoromethyl)propane. 1,1,1,3,3,3-Hexafluoro-2-(fluoromethyl)propane (34 g) was added to a suspension of 20 g of KOH powder in 20-25 ml of dibutyl ether; after the addition the reaction mixture was heated for 20-30 minutes at 40-50° under reflux. The reaction products were then distilled off into a trap cooled to − 60°. After distillation we obtained 21.5 g (70%) of 3,3,3-trifluoro-2-(trifluoromethyl)propene, b. p. 13-14° [6]. Found %: C 29.46; H 1.30; F 69.90; mol. wt. 164. $C_4H_2F_6$. Calculated %: C 29.26; H 1.15; F 69.51; mol. wt. 164.

Dehydrofluorination of 1,1,1,3,3,3-Hexafluoro-2-methylpropane. 40-50 g of 90% KOH was placed in a U-tube and melted by heating it to 170-172° in a glycerol bath. Gaseous 1,1,1,3,3,3-hexafluoro-2-methylpropane (34 g) was passed slowly through the melt, and the reaction products were collected in a cooled trap and then again passed through the alkali melt 2-3 times. As a result of the reaction we obtained 20 g of substance, from which by distillation through a column we isolated 6 g of unchanged 1,1,1,3,3,3-hexafluoro-2-methylpropane and 13.2 g (54% on the 1,1,1,3,3,3-hexafluoro-2-methylpropane that reacted) of 1,1,3,3,3-pentafluoro-2-methylpropene, b. p. 12-13°. For 1,1,3,3,3-pentafluoro-2-methylpropene the literature [6, 13] gives b. p. 13.8°. Found %: C 32.07; H 2.04; F 65.96; mol. wt. 147. $C_4H_3F_5$. Calculated %: C 32.87; H 2.05; F 65.06; mol. wt. 146.

Dehydrofluorination of 1,1,1,2,3,3-Hexafluoropropane. 1,1,1,2,3,3-Hexafluoropropane (24 g) was passed slowly into a suspension of 18 g of KOH powder in 15 ml of dibutyl ether with stirring and cooling with ice water. Reaction occurred with evolution of heat, and the reaction products liberated were collected in a trap cooled to − 70°. We obtained 17.3 g of substance, from which by distillation we isolated 3.5 g of unchanged 1,1,1,2,3,3-hexafluoropropane, b. p. 4-5°, and 12.8 g (60%) of 1,2,3,3,3-pentafluoropropene ($CF_3CF=CFH$), b. p. − 20°. Found %: C 27.21; H 0.79; F 71.71; mol. wt. 132.5. C_3HF_5. Calculated %: C 27.27; H 0.75; F 71.96; mol. wt. 132.

Hydrogenation of 1,2,3,3,3-pentafluoropropene. A mixture of 23 g of gaseous 1,2,3,3,3-pentafluoropropene and hydrogen (2:3 by volume) was passed over 1% Pd/Al_2O_3 at room temperature. The hydrogenation products were collected in a cooled trap and distilled through a column. We obtained 13.2 g (60%) of 1,1,1,2,3-pentachloropropane, b. p. 20°. NMR (nuclear magnetic resonance spectrum): δ 7,15 (CF_3); 20,59 (CFH); 23,46 (CFH_2). Found %: C 26.88; H 2.59; F 70.22; mol. wt. 134.5. $C_3H_3F_5$. Calculated %: C 26.84; H 2.23; F 70.88; mol. wt. 134. We isolated also 6.6 g (about 30%) of 1,1,1,2-tetrachloropropane, b. p. − 1°. Found %: C 30.71; H 3.95; mol. wt. 115. $C_3H_4F_4$. Calculated %: C 31.03; H 3.44; mol. wt. 116.

Dehydrofluorination of 1,1,1,2,3-Pentafluoropropane. 1,1,1,2,3-Pentafluoropropane (20 g) was added with stirring to a suspension of 20 g of KOH in dibutyl ether. The reaction products were collected in a trap cooled to − 78°, and were then passed again through the suspension of alkali. Distillation of the reaction products through a column gave 11.5 g (70%) of 2,3,3,3-tetrafluoropropene, b. p. − 28° [7].

Hydrogenation of 1,1,3,3,3-Pentafluoropropene. A mixture of 20 g of gaseous 1,1,3,3,3-pentafluoropropene and hydrogen (2:3 by volume) was passed over 1% Pd/Al_2O_3 at room temperature. Distillation of the reaction products gave 16 g (70% on the 1,1,3,3,3-pentafluoropropene taken) of 1,1,1,3,3-pentafluoropropane, b. p. 12°. NMR: δ 5,57 (CF_3); 10,72 (CF_2H) * Found %: C 27.03; H 2.05; F 70.43; mol. wt. 135. $C_3H_3F_5$. Calculated %: C 26.84; H 2.23; F 70.88; mol. wt. 134.

Dehydrofluorination of 1,1,1,3,3-Pentafluoropropane. 1,1,1,3,3-Pentafluoropropane (15 g) was passed twice through a suspension of 20 g of KOH powder in dibutyl ether. The condensed reaction product was distilled through a column and gave 9 g (70%) of 1,3,3,3-tetrafluoropropene, b. p. − 16° [8, 9].

Hydrogenation of Perfluorobutadiene. A mixture (20 liters) of perfluorobutadiene and hydrogen (ratio 1:4 by volume) was passed over 15 g of 1% Pd/Al_2O_3 at room temperature. The reaction gave 20 g (66%) of 1,1,2,3,4,4-hexafluorobutane [16], b. p. 63-65° and $n^{20}D$ 1.2985.

Dehydrofluorination of 1,1,2,3,4,4-Hexafluorobutane. 1,1,2,3,4,4-Hexafluorobutane (11 g) was refluxed for 1-1.5 hours in presence of KOH powder (25-30 g); the reaction products were then distilled off through a column. We obtained 8.5 g (85%) of 1,1,2,4,4-pentafluoro-2-butene, b. p. 56° and $n^{20}D$ 1.306. Found %: C 32.76; H 2.24; F 64.91. $C_4F_5H_3$. Calculated %: C 32.87; H 2.04; F 65.06.

* The spectra of nuclear magnetic resonance (NMR) of F^{19} were determined at the Radiotechnics Department of the Physics Faculty of the Moscow State University by Yu. S. Konstantinov. The resonance frequency of the supporting sample (CF_2Cl_2) was 18.25 MHz. The relative chemical displacement was calculated from the formula $\delta = \Delta f / f_{support} \cdot 10^5$, in which f is the resonance frequency.

Oxidation of 1,1,2,4,4-Pentafluoro-2-butene. With passage of carbon dioxide, 15 g of 1,1,2,4,4-pentafluoro-2-butene was added gradually to a solution of 50 g of potassium permanganate in 250 ml of water at room temperature; reaction occurred with evolution of heat; stirring was continued for 4-4.5 hours. The reaction mixture was then stirred further for 5-6 hours with passage of carbon dioxide and warming to 60-70°. Sulfur dioxide was passed through the cooled solution until colorless, and the precipitate was filtered off. The filtrate was placed in a continuous extractor and extracted with ether for 24 hours. The ether solution was dried and distilled; we isolated 7.6 g (40%) of difluoroacetic acid, b. p. 128-130°. The acid was identified as its aniline salt, m. p. 78°, undepressed by admixture of the aniline salt prepared from pure difluoroacetic acid.

Bromination of 1,1,2,4,4-Pentafluoro-2-butene. Bromine (3 ml) was added to a solution of 8 g of 1,1,2,4,4-pentafluoro-2-butene in 10 ml of glacial acetic acid, and the mixture was heated in a sealed tube in a boiling water bath. The reaction solution was washed with sodium bicarbonate solution and with water, and it was dried with anhydrous magnesium sulfate. Distillation gave 9.5 g (about 45%) of the dibromide, b. p. 146-148°. Found %: C 16.00; H 1.07; F 31.46. $C_4H_3F_5Br_2$. Calculated %: C 15.69; H 0.98; F 31.06.

SUMMARY

1. It is shown that perfluoro olefins may be catalytically hydrogenated. Perfluoroethylene, perfluoropropene, perfluoroisobutene, and other fluoro olefins were hydrogenated over nickel and palladium catalysts.

2. In hydrogenation over a nickel catalyst, in addition to the normal products of hydrogen addition, products resulting from the further replacement of fluorine by hydrogen are formed. Over a palladium catalyst products of normal hydrogenation are formed almost exclusively.

3. By the catalytic hydrogenation of perfluoro olefins with subsequent dehydrofluorination, various ethylene, propene, and isobutene derivatives containing different amounts of fluorine were synthesized.

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SYNTHESIS OF ALKENYLSILANES BY THE ADDITION OF DICHLOROMETHYLSILANE TO DIENIC AND ACETYLENIC COMPOUNDS

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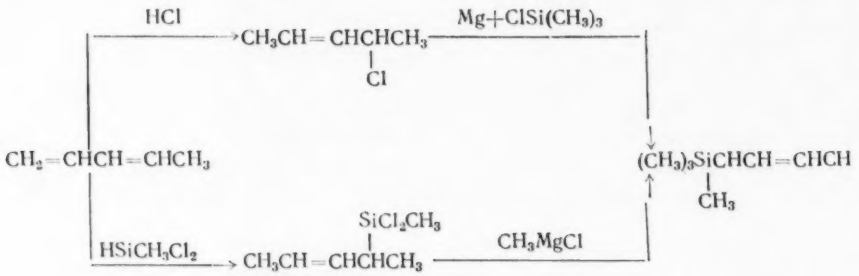
One possible method of synthesizing unsaturated organosilicon compounds is the addition of compounds containing silicon-attached hydrogen to dienic and acetylenic compounds. However, this method with dienes as basis [1-8] has been used for the synthesis of only a few compounds; 1,4-addition has been established only for butadiene [1, 3] for the cases of trichloro-, dichloromethyl-, and dichloroethyl-silanes (in presence of a platinized charcoal catalyst):

$$CH_2=CH-CH=CH_2 + HSiCl_3 \xrightarrow{Pt/C} CH_3CH=CHCH_2SiCl_3.$$

In the present work we have shown that dichloromethylsilane adds to piperylene (in presence of Speier's catalyst [9]), again with 1,4-addition. The structure of the product was proved by carrying out reactions according to the scheme:



It was shown that the two samples of trimethyl(1-methyl-2-butenyl)silane synthesized by these two different methods were identical on the basis of the coincidence of their Raman spectra.

The addition of dichloromethylsilane to a nonconjugated diene, 1,5-hexadiene, proceeds fairly vigorously, but in addition to the expected dichloro-5-hexenylmethylsilane we obtained a dichlorohexenylmethylsilane in which the double bond was in a different position with respect to the silicon atom, which was established after methylation and analysis of the Raman spectra. The use in the present work of the almost homogeneous Speier catalyst [9] instead of platinized charcoal enabled us to avoid severe reaction conditions, which necessitate the use of autoclaves, and we were able to carry out all additions of dichloromethylsilane to dienic and acetylenic compounds at atmospheric pressure by boiling the reactants in an ordinary flask. As regards the addition of

silanes containing silicon-attached hydrogen to acetylene derivatives, extremely few examples are cited in the literature [10-16], and in most cases no proof is given of the structure of the products.

In the present work we carried out the addition of dichloromethylsilane to ethynylbenzene, hexyne, ethylethynyldimethylsilane, and ethynyl isopropyl ether. The direction of addition to ethynylbenzene was proved by comparison of the Raman spectrum of the resulting β-(trimethylsilyl)styrene [trimethylstyrylsilane] with that of the known α-(trimethylsilyl)styrene, which we prepared previously [17]:

$$C_6H_5C{\equiv}CH + HSiCl_2CH_3 \longrightarrow C_6H_5CH{=}CHSiCl_2CH_3 \xrightarrow{CH_3MgCl} C_6H_5CH{=}CHSi(CH_3)_3.$$

For the purpose of comparison we also synthesized trimethylstyrylsilane by the organomagnesium method proposed by Sommer [18]:

$$C_6H_5CH{=}CHMgBr + ClSi(CH_3)_3 \longrightarrow C_6H_5CH{=}CHSi(CH_3)_3.$$

However, we did not succeed in obtaining pure trimethylstyrylsilane by this method: according to the Raman spectra some $C_6H_5C{\equiv}CSi(CH_3)_3$. was always present.

To 1-hexyne, dichloromethylsilane added with formation of dichloro-1-hexenylmethylsilane, which was again established by analysis of Raman spectra:

$$C_4H_9C{\equiv}CH + HSiCl_2CH_3 \longrightarrow C_4H_9CH{=}CHSiCl_2CH_3 \longrightarrow C_4H_9CH{=}CHSi(CH_3)_3.$$

The addition of dichloromethylsilane to ethylethynyldimethylsilane led to the formation of compounds with all the characteristic features (high exaltation of MR [19] and specific features of Raman spectra [20]) of 1,2-disilylethylenes [21]:

$$C_2H_5(CH_3)_2SiC{\equiv}CH + HSiCH_3Cl_2 \longrightarrow$$

$$\longrightarrow C_2H_5(CH_3)_2SiCH{=}CHSiCH_3Cl_2 \xrightarrow{CH_3MgCl} C_2H_5(CH_3)_2SiCH{=}CHSi(CH_3)_3.$$

EXPERIMENTAL

Dichloromethyl(1-methyl-2-butenyl)silane $Cl_2CH_3SiCH(CH_3)CH{=}CHCH_3$. A portion (15 ml) of a mixture of 112 g of dichloromethylsilane, 65 g of piperylene, and 1 ml of Speier's catalyst [9] (0.1 N $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol) was warmed in a flask fitted with reflux condenser and thermometer. When reaction set in (rise in boiling point), the remainder of the mixture was added in such a way that the temperature in the flask did not rise above 100-120°. After a five-hour boil, distillation through a column gave 75 g (43 %) of dichloromethyl(1-methyl-2-butenyl)silane; b. p. 163-165°; $n^{20}D$ 1.4517, d^{20}_0 1.0285; found MR 48.01; calculated MR 47.6.

Trimethyl(1-methyl-2-butenyl)silane $(CH_3)_3SiCH(CH_3)CH{=}CHCH_3$ A. A mixture of 108 g of chlorotrimethylsilane and 150 g of 3-chloro-2-pentene was added over a period of five hours to 48 g of magnesium in 1200 ml of dry ether [22]. After a ten-hour boil the contents of the flask were decomposed with water. The ether layer, together with ether extracts of the water layer, was dried with calcium chloride. Fractionation through a column gave 72 g (51%) of trimethyl(1-methyl-2-butenyl)silane; b. p. 131.5° (746 mm); $n^{20}D$ 1.4285, d^{20}_4 0.7523; found MR 48.72; calculated MR 48.33. Found %: C 67.41, 67.40; H 12.86, 12.97; Si 19.64, 19.62. $C_8H_{12}Si$. Calculated %: C 67.60; H 12.68; Si 19.72.

In addition, we isolated 32 g of a fraction which did not contain silicon; b. p. 151-151.5° (746 mm); $n^{20}D$ 1.4385, d^{20}_4 0.7604. This was probably the diene $C_{10}H_{18}$. Found %: C 86.01, 85.80; H 13.17, 13.21. $C_{10}H_{18}$. Calculated %: C 86.87; H 13.12.

B. To CH_3MgCl, prepared from 25 g of magnesium in 500 ml of ether, we added [here a line of the original text is omitted] the contents of the flask were decomposed with water, and after the usual treatments we isolated, by the use of a column, 29 g (50%) of trimethyl(1-methyl-2-butenyl)silane; b. p. 133-134°; $n^{20}D$ 1.4260, d^{20}_4 0.7505; found MR 48.50; calculated MR 48.33.

Raman spectrum: 153 (2), 242 (3 b), 299 (0 b), 362 (3 sh), 391 (0), 448 (2), 477 (3), 556 (4 b, db), 605 (10 b), 695 (5 b), 752 (0), 805 (1), 845 (1), 853 (1 b), 967 (0 b), 1041 (1 b), 1105 (0 b), 1163 (5 v.b.), 1255 (4 b), 1308 (4 b), 1376 (3 sh), 1415 (2 b), 1460 (4 b), 1662 (10), 2900 (10), 2961 (10), 3009 (1).

The spectrum obtained was substantially coincident with that of the same substance prepared by Method A.

Addition of Dichloromethylsilane to 1,5-Hexadiene. Dichloromethylsilane (131 g) was added to 100 g of 1,5-hexadiene containing 0.5 ml of Speier's catalyst at such a rate that the temperature did not rise above about 70°. By vacuum distillation we isolated 132 g (55%) of substance; b. p. 112-113° (75 mm); $n^{20}D$ 1.4523, d^{20}_4 1.0067; found MR 52.87; calculated MR 52.22. In addition we isolated 42 g of substance that came over at 210-211° (product of the addition of two molecular proportions of $HSiCl_3$). Methylation of 80 g of the fraction of b. p. 112-113° (75 mm) was carried out with CH_3MgCl prepared from 24 g of magnesium in 1 liter of ether. After the usual treatments fractionation through a column gave 39 g (61%) of hexenyltrimethylsilane; b. p. 112-113° (75 mm), $n^{20}D$ 14.523, d^{20}_4 1.0067, found MR 52.87; calculated MR 52.22; MR 52.96. In the Raman spectra of this substance we found two frequencies of equal intensity attributable to the double bond (1639 and 1672 cm^{-1}). The first frequency is characteristic for a double bond at the end of a chain, and the second for a double bond in the middle of the chain.

Dichloromethylstyrylsilane $C_6H_5CH=CHSiCl_2CH_3$. A mixture of 24.5 g of ethynylbenzene, 28.2 g of dichloromethylsilane, and 0.5 ml of Speier's catalyst was heated until the temperature rose to 180° (four hours). Vacuum fractionation gave 30 g (58%) of dichloromethylstyrylsilane; b. p. 127° (20 mm); $n^{20}D$ 1.5477, d^{20}_4 1.1634; found MR 59.45; calculated MR 59.31. Found %: Si 12.64, 12.94. $C_9H_{10}SiCl_2$. Calculated %: Si 12.66.

Trichlorostyrylsilane $C_6H_5CH=CHSiCl_3$. Under the conditions of the preceding experiment, from 35.5 g of ethynylbenzene and 50 g of trichlorosilane we obtained 52 g (61%) of trichlorostyrylsilane; b. p. 133° (10 mm); $n^{20}D$ 1.5575, d^{20}_4 1.2848; found MR 59.58; calculated MR 59.94.

Trimethylstyrylsilane $C_6H_5CH=CHSi(CH_3)_3$. Dichloromethylstyrylsilane (29 g) was added to CH_3MgCl prepared from 7 g of magnesium in 200 ml of ether. After the usual treatments vacuum fractionation gave 17 g (72%) of trimethylstyrylsilane; b. p. 96-97° (12 mm); $n^{20}D$ 1.5214; d^{20}_4 0.8886; found MR 60.45; calculated MR 60.41.

Raman spectrum: 148 (1), 175 (0), 197 (1), 232 (1), 301 (0), 406 (0), 570 (4), 613 (1), 622 (5), 695 (2), 729 (1), 823 (3 b), 1001 (9), 1030 (3), 1155 (2), 1175 (4 b), 1215 (10), 1248 (0 b), 1304 (1), 1332 (4), 1405 (0), 1444 (2), 1492 (2 b), 1574 (5 sh), 1603 (20), 2895 (6 b), 2955 (5), 3054 (2).

$C_6H_5C(CH_2)Si(CH_3)_3$: Raman spectrum: 148 (2), 194 (0), 240 (0), 297 (0), 432 (1), 508 (0), 611 (8), 622 (1), 692 (1 b), 783 (0), 840 (1), 973 (0), 1000 (10), 1030 (2), 1066 (0), 1101 (2), 1156 (1), 1178 (1 b), 1231 (4 b), 1251 (0), 1285 (0 b), 1398 (3 b), 1488 (1 b), 1571 (2), 1599 (10), 2896 (5 b), 2958 (4 b), 2992 (0), 3057 (1).

Dichloro-1-hexenylmethylsilane $CH_3CH_2CH_2CH_2CH=CHSiCl_2$. A mixture of 13 g of 1-hexyne, 20 g of dichloromethylsilane, and 1 ml of Speier's catalyst was boiled for 30 hours. Vacuum distillation gave 9 g (28%) of dichloro-1-hexenylmethylsilane; b. p. 82.5° (17 mm); $n^{20}D$ 1.4492; d^{20}_4 1.0196; found MR 51.68; calculated MR 52.22. Found %: Si 14.21, 13.94. $C_7H_{14}SiCl_2$. Calculated %: Si 14.24.

1-Hexenyltrimethylsilane $CH_3CH_2CH_2CH_2CH=CHSi(CH_3)_3$. Dichloro-1-hexenylmethylsilane (13.5 g) was added to CH_3MgCl prepared from 5 g of magnesium in 200 ml of ether. After a three-hour boil and the usual treatments, with the aid of a column we obtained 6.7 g (62%) of 1-hexenyltrimethylsilane; b. p. 159°; $n^{20}D$ 1.4225; d^{20}_4 0.7549; found MR 52.67; calculated MR 52.96.

Ethylethynyldimethylsilane [23] $CH\equiv CSi(CH_3)_2C_2H_5$. Acetylene was bubbled through 200 ml of tetrahydrofuran in a 1.5 liter flask fitted with stirrer, reflux condenser, and dropping funnel, and simultaneously addition was made of ethylmagnesium bromide prepared from 24 g of magnesium and 108 g of ethyl bromide in 300 ml of tetrahydrofuran. The addition of C_2H_5MgBr was made in 8 ml portions at intervals of 5 minutes, and for this four hours was required. To the ethynylmagnesium bromide so formed we added 50 g of chloroethyldimethylsilane, and the contents of the flask were boiled for 15 hours, with an overnight break. After decomposition with water and the usual treatments, fractionation through a column gave 38 g (83.5%) of ethylethynyldimethylsilane; b. p. 83.2° (751 mm); $n^{20}D$ 1.4082; d^{20}_4 0.7435; found MR 37.26; calculated MR 37.81. Found %: C 64.24, 64.19; H 10.73, 10.58; Si 24.90, 24.72. $C_6H_{12}Si$. Calculated %: C 64.20; H 10.77; Si 25.02.

Raman spectrum: 144 (6 b), 221 (3 b), 248 (1), 272 (1), 292 (2), 314 (0), 350 (2), 387 (2), 422 (0), 457 (2), 491 (0), 546 (6), 566 (3), 640 (4), 675 (2 b), 700 (31 b), 786 (3 b), 911 (1), 976 (2), 1019 (3 b), 1129 (0), 1149 (0 b), 1201 (0 b), 1242 (2), 1259 (2), 1410 (4 b), 1461 (3 b), 2060 (10), 2880 (4), 2904 (8), 2938 (2), 2964 (8), 3260 (2).

1-(Ethyldimethylsilyl)-2-(trimethylsilyl)ethylene $C_2H_5(CH_3)_2SiCH=CHSiCl_2CH_3$. To 26 g of ethylethynyldimethylsilane we added 0.5 ml of Speier's catalyst and about 5 ml (of a total amount of 27 g) of dichloromethylsilane. Gentle warming of the mixture for a few minutes prompted the onset of vigorous reaction with boiling. The remainder of the dichloromethylsilane was added with stirring at such a rate that the temperature of the contents of the flask did not rise above about 90°. Vacuum distillation on the next day gave 28 g (53%) of $Cl_2CH_3SiCH=CHSi(CH_3)_2C_2H_5$ b. p. 104° (45 mm); $n^{20}D$ 1.4590; d^{20}_4 0.9861; found MR 62.73; calculated MR 61.73.

1-(Ethyldimethylsilyl)-2-(trimethylsilyl)ethylene $C_2H_5(CH_3)_2SiCH=CHSi(CH_3)_3$. To CH_3MgCl prepared from 10 g of magnesium in 320 ml of ether we added 26 g of $Cl_2CH_3SiCH=CHSi(CH_3)_2C_2H_5$. After a two-hour boil and the usual treatments, fractionation through a column gave 16.5 g (77.2%) of $(CH_3)_3SiCH=CHSi(CH_3)_2C_2H_5$ b. p. 166° (762 mm); $n^{20}D$ 1.4380, d^{20}_4 0.7730; found MR 63.32; calculated MR 62.33.

Raman spectrum: 148 (2), 185 (3 b), 231 (3 b), 284 (1), 326 (2), 364 (0), 593 (5), 609 (10), 640 (0), 674 (1), 696 (5 b), 771 (0 b), 795 (1 b), 843 (2 b), 974 (1 b), 1017 (2 b), 1140 (2 b), 1198 (3 b), 1230 (2), 1254 (3), 1297 (6), 1323 (0), 1382 (0), 1417 (3 b), 1464 (2 b), 1557 (4 b), 2898 (10 b), 2961 (10).

The determination and analysis of Raman spectra were carried out by L. Leites, to whom we express our thanks.

SUMMARY

1. In presence of Speier's catalyst dichloromethylsilane adds to piperylene in the 1,4-positions with formation of dichloromethyl (1-methyl-2-butenyl)silane.

2. The addition of CH_3SiCl_2H to various monosubstituted derivatives of acetylene proceeds in such a way that the silyl group adds exclusively to the hydrogenated carbon atom participating in the triple bond.

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NITRATION OF AROMATIC SILA-HYDROCARBONS IN WHICH THE AROMATIC RING OCCUPIES VARIOUS POSITIONS WITH RESPECT TO THE SILICON ATOM

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No. 8, pp. 1424-1428, August, 1960
Original article submitted March 13, 1959

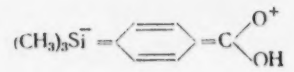
Despite the considerable lability of the $Si-C_{aryl}$ bond toward electrophilic reagents, various compounds of formula $R_3Si-C_6H_5$ have been successfully nitrated by various investigators. Already in 1935, Kipping and Cusa [1] reported the nitration of phenylsilanes with nitric acid in a solvent in the cold. Dolgov and Panina [2] nitrated triethylphenylsilane with fuming nitric acid diluted tenfold with acetic anhydride at 0°. However, these authors did not separate the o-, m-, and p-isomers. Recently, Speier [3] nitrated trimethylphenylsilane with fuming nitric acid in acetic anhydride at 25-70° and 0-10°. All the isomers were separated by precision fractionation, and the relative amounts of o-, m-, and p-isomers were 26.6 : 41.7 : 31.6 at 0-10° and 32.5 : : 34.7 : 32.7 at 25-70°. The nitration was quantitative, but trimethylphenylsilane was split to the extent of about 10% by nitric acid at the $Si-C_{aryl}$ bond with formation of nitrobenzene. Hence, the trimethylsilyl group in trimethylphenylsilane is a feeble ortho-para orientant, i.e., is a feebly electron-donating group. The feebleness also of the orienting effect of the triethylsilyl group is indicated by the fact that in the nitration of triethyltolylsilane the determining factor in the introduction of the nitro group in one or other position is the position of the methyl group [4]. The nitration of aromatic sila-hydrocarbons can be carried out also with copper nitrate in acetic anhydride [5], but in this case, with approximately the same relative amounts of isomers, the percentage splitting of the $Si-C_{aryl}$ bond is doubled. By this method both trimethylphenylsilane and benzyltrimethylsilane have been nitrated [5].

Hence, by the action of nitric acid on trialkylphenylsilanes attack of the latter is possible both at the C–H bonds of the aromatic nucleus and at the $Si-C_{aryl}$ bond. However, the rate of the first reaction is higher than that of the second, and when a strongly electron-accepting substituent, such as the NO_2 group (Hammett's constant $\sigma^p_{NO_2} = 0.778$; $\sigma^m_{NO_2} = 0.710$) [6], is present, the $Si-C_{aryl}$ bond is fairly stable to the action of nitric acid, which is a condition for successful nitration.

The possibility of the $Si-C_{aryl}$ bond to be split under the action of nitric acid with formation of the nitroarene and the silanol [3, 5, 7] was utilized by Deans and Eaborn [8] in the preparation of (nitrophenyl) silanes with the nitro group in a defined position. Thus, by the splitting of p-bistrimethylsilylbenzene with nitric acid, an 82 % yield was obtained of trimethyl(p-nitrophenyl)silane. This method is undoubtedly of interest for the synthesis of substituted nitroarenes.

For the nitration of a mixture of trimethylphenylsilane and benzene Speier [3], using the method of "competing" reactions, determined the relative activities of the o-, m-, and p-positions in trimethylphenylsilane, which were found to be 1.3 : 2.0 : 3.1, if the activity of any C–H bond of benzene is taken as 1. This again confirms the electron-donor character of the trimethylsilyl group, and it is in good accord with the diminution in the strengths of acetic and propionic acids on replacement of hydrogen in the α- or β-position

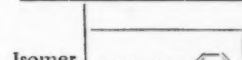
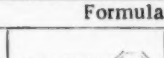
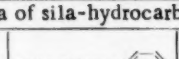
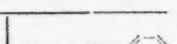
to the carboxy group by $(CH_3)_3Si$ [9]. However, Speier's results are in conflict with those of Chaff and Williams [10], who showed that p-(trimethylsilyl)benzoic acid is a stronger acid than benzoic, i.e., that in this case the trimethylsilyl group behaves as an electron acceptor. The authors explain this fact on the view that $Si-C_{aryl}$ in p-(trimethylsilyl)benzoic acid has the character of a double bond because of the displacement of the π-electron cloud of the aromatic ring toward the silicon atom and a consequent reduction in the electron density of the ring



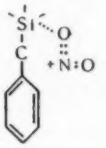
In the case of trimethylphenylsilane this phenomenon is evidently not observed.

Our task in the present investigation was the nitration of mixtures of sila-hydrocarbons $(CH_3)_3Si(CH_2)_nC_6H_5$ (n = 1, 2, 3, 4) with benzene by the method of "competing" reactions with the object of determining the proportions of isomers, and also the relative activities of these sila-hydrocarbons in the o-, m-, and p-positions with respect to benzene, in which the activity of each C–H bond is taken as 1. The nitration was carried out with fuming nitric acid in acetic anhydride at 0°. In the fractionation of the products nitrotoluene, ethylnitrobenzene, nitropropylbenzene, and butylnitrobenzene, respectively, were not detected; hence, splitting of the Si–C bond did not occur. The yields of nitro derivatives were 54-74%. On nitration of benzyltrimethylsilane with copper nitrate the total yield of nitro derivatives was 64%. In all cases only o- and p-isomers were obtained. In Table 1 we give the relative amounts (%) of isomers obtained in all cases.

TABLE 1

Isomer	Formula of sila-hydrocarbon				
	 with $Cu(NO_3)_2 \cdot 3H_2O$	 with HNO_3	 with HNO_3	with HNO_3	 with HNO_3
Ortho	78,1	85,0	45,8	49,2	64,9
Para	21,9	15,0	54,2	50,8	35,1

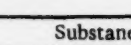
The very high amount of o-isomer obtained in the nitration of benzyltrimethylsilane is noteworthy. This is clearly not accidental. It is generally known that organosilicon compounds can give complex compounds; with a valence of four the coordination number of silicon is six. It is probable that the sila-hydrocarbon molecule and the nitronium ion form a reaction complex in which the silicon atom is attached to an oxygen of the nitronium ion:



In such a complex, attack of the o-position is undoubtedly facilitated, which explains the large amount of o-isomer.

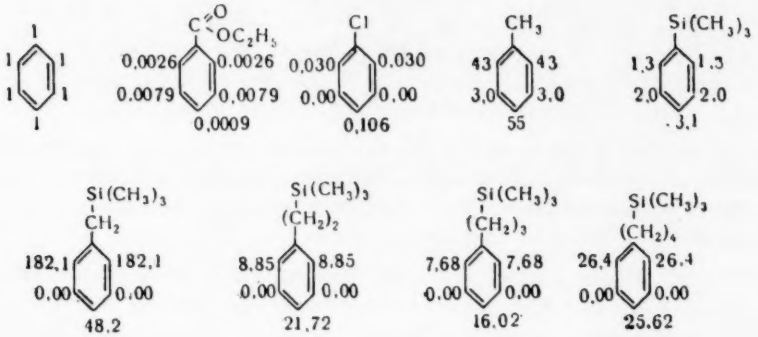
Interesting results were obtained in the determination of the relative activities of the aromatic rings of the compounds under investigation by Ingold's method [11]. These results are given in Table 2.

TABLE 2

Ratio of	Substance					
						
K of substance to K of benzene	1	1,64	77,2	8,87	10,62	18,96

As will be seen from Table 2, in the series $(CH_3)_3Si(CH_2)_n$– an unusually high reactivity is possessed by the compound for which n = 1, i.e., that in which the aromatic ring is in the β-position to the silicon atom. Such a sharp increase in the reactivity of this compound cannot be explained solely by the inductive effect of the substituent, for in that case one should observe a monotonic rise in the reactivity of compounds in the homologous series as we pass from the compound with n = 0 to that with n = 1, and that with n = 2, etc.

Neither do steric factors play a great part in this homologous series. Hence, we here observe the phenomenon of conjugation of an Si–C bond with an aromatic ring in the β-position, analogous to the phenomenon of conjugation of an Si–C bond with a double bond or with a C–Cl bond in the γ-position [12-15]. Determinations were made, also by Ingold's method, of the relative reactivities of the o-, m-, and p-positions in the sila-hydrocarbons studied. By the use also of data in the literature [3, 16] we may give the following interesting series:



EXPERIMENTAL

Nitration of Benzyltrimethylsilane and Benzene with Nitric Acid. A mixture of 78 g (1 mole) of benzene, 164 g (1 mole) of benzyltrimethylsilane, and 107 g of acetic anhydride was prepared in a flask fitted with reflux condenser and dropping funnel. The reaction mixture was cooled to − 10°. A mixture of 75 g (1.05 moles) of 90% fuming nitric acid and 152 g of acetic anhydride was also cooled to − 10°, and at this temperature it was dropped slowly over a period of 2.5 hours into the reaction flask. After the addition of the whole of the nitric acid the mixture was kept at − 10° for a further 2.5 hours and was then placed in a refrigerator overnight. After 14 hours, the temperature of the mixture was − 1°. The contents of the flask were poured into a mixture of ice and 28% ammonia. The organic layer was dried with calcium chloride and fractionated. On fractionation we isolated: 1) 75.8 g (0.972 mole) of benzene, b. p. 79.5-80° (754 mm); 2) 58.1 g (0.360 mole) of benzyltrimethylsilane, b. p. 191-192° (754 mm) and $n^{20}D$ 1.5038; 3) 1.3 g (0.0106 mole) of nitrobenzene, b. p. 74-75.5° (10 mm) and $n^{20}D$ 1.5520; 4) 99.8 g (0.477 mole) of trimethyl(o-nitrobenzyl)silane, b. p. 121° (10 mm), $n^{20}D$ 1.5260, and d^{20}_4 1.0460; the literature [5] gives b. p. 125° (10 mm), $n^{20}D$ 1.5276,

and d^{20}_4 1.045; 5) 17.5 g (0.084 mole) of trimethyl(p-nitrobenzyl)silane, b. p. 142° (10 mm), $n^{20}D$ 1.5428, and n^{20}_4 1.0700; the literature [5] gives b. p. 147° (10 mm), $n^{20}D$ 1.5423, and d^{20}_4 1.069. The residue amounted to 18.9 g.

Nitration of Trimethylphenethylsilane and Benzene with Nitric Acid. The reaction conditions were strictly identical with those used in the preceding experiment. For reaction we took a mixture of 78 g (1 mole) of benzene, 178 g (1 mole) of trimethylphenethylsilane, and 107 g of acetic anhydride. As nitration mixture we used a mixture of 75 g (1.05 moles) of 90% fuming nitric acid and 152 g of acetic anhydride. In the fractionation we isolated: 1) 68.3 g (0.876 mole) of benzene, b. p. 78-79.5° (748 mm); 2) 48.4 g (0.272 mole) of trimethylphenethylsilane, b. p. 77-78° (7.5 mm) and $n^{20}D$ 1.4874; 3) 14.2 g (0.116 mole) of nitrobenzene, b. p. 74-76° (10 mm) and $n^{20}D$ 1.5525; 4) 68.0 g (0.305 mole) of trimethyl(o-nitrophenethyl) silane, b. p. 118-119° (5 mm), $n^{20}D$ 1.5124, and d^{20}_4 1.0254. Found %: C 58.98, 58.83; H 7.58, 7.46; Si 12.35, 12.48. $C_{11}H_{17}SiNO_2$. Calculated %: C 59.19; H 7.62; Si 12.55. 5) 80.2 g (0.360 mole) of trimethyl(p-nitrophenethyl)silane, b. p. 135° (5 mm), $n^{20}D$ 1.5211, and d^{20}_4 1.0271. Found %: C 58.75, 59.11; H 7.68, 7.73; Si 12.24, 12.36. $C_{11}H_{17}SiNO_2$. Calculated %: C 59.19; H 7.62; Si 12.55. The residue amounted to 14.8 g.

Nitration of Trimethyl(3-phenylpropyl)silane and Benzene with Nitric Acid. Trimethyl(3-phenylpropyl) silane was synthesized by the addition of trichlorosilane to (2-propenyl)benzene in presence of H_2PtCl_6 with subsequent methylation of the addition product with CH_3MgBr; it had the following properties: b. p. 56° (2 mm); $n^{20}D$ 1.4853, and d^{20}_4 0.8684.

For reaction we took a mixture of 78 g (1 mole) of benzene, 192 g (1 mole) of trimethyl(3-phenylpropyl) silane, and 107 g of acetic anhydride. The nitration mixture was a mixture of 75 g (1.05 moles) of 90% fuming nitric acid and 152 g of acetic anhydride. The reaction conditions were strictly the same as in the first experiment. In the fractionation we isolated: 1) 66.1 g (0.847 mole) of benzene, b. p. 78-79.5° (749 mm); 2) 17.5 g (0.142 mole) of nitrobenzene, b. p. 99-101° (27 mm) and $n^{20}D$ 1.5518; 3) 42.8 g (0.223 mole) of trimethyl(3-phenylpropyl)silane, b. p. 90-91° (7 mm) and $n^{20}D$ 1.4850; 4) 86.6 g (0.366 mole) of trimethyl(3-o-nitrophenylpropyl)silane, b. p. 130-131° (5 mm), $n^{20}D$ 1.5085, and d^{20}_4 1.0098. Found %: C 60.62, 60.68; H 8.06, 8.10; Si 11.56, 11.48. $C_{12}H_{19}SiNO_2$. Calculated %: C 60.76; H 8.02; Si 11.81. 5) 89.7 g (0.378 mole) of trimethyl(3-p-nitrophenylpropyl)silane, b. p. 140° (5 mm), $n^{20}D$ 1.5151, and d^{20}_4 1.0112. Found %: C 60.88, 60.85; H 7.98, 8.02; Si 11.80, 11.89. $C_{12}H_{19}SiNO_2$. Calculated %: C 60.76; H 8.02; Si 11.81. The residue amounted to 6.4 g.

Nitration of Trimethyl(4-phenylbutyl)silane and Benzene with Nitric Acid. Trimethyl(4-phenylbutyl) silane was synthesized by the addition of trichlorosilane to (3-butenyl)benzene in presence of H_2PtCl_6 with subsequent methylation of the addition product with CH_3MgBr; it had the following properties: b. p. 91-92° (3 mm); $n^{20}D$ 1.4828, and d^{20}_4 0.8656.

For reaction we took a mixture of 78 g (1.0 mole) of benzene, 206 g (1.0 mole) of trimethyl(4-phenylbutyl)silane, and 107 g of acetic anhydride. The nitration mixture was a mixture of 75 g (1.05 moles) of 90% fuming nitric acid and 152 g of acetic anhydride. The reaction conditions were strictly the same as in the first experiment. In the fractionation we isolated: 1) 72.8 g (0.933 mole) of benzene, b. p. 78-80° (750 mm); 2) 6.1 g (0.048 mole) of nitrobenzene, b. p. 95-96° (20 mm), and $n^{20}D$ 1.5520; 3) 76.1 g (0.369 mole) of trimethyl(4-phenylbutyl)silane, b. p. 93° (4 mm) and $n^{20}D$ 1.4870; 4) 88.7 g (0.352 mole) of trimethyl-(4-o-nitrophenylbutyl)silane, b. p. 135° (5 mm), $n^{20}D$ 1.5048, and d^{20}_4 1.0003. Found %: C 62.14, 61.95; H 8.54, 8.23; Si 11.29, 11.65. $C_{13}H_{21}SiNO_2$. Calculated %: C 62.15; H 8.37; Si 11.15. 5) 47.5 g (0.190 mole) of trimethyl(4-p-nitrophenylbutyl)silane, b. p. 149° (5 mm), $n^{20}D$ 1.5116, and d^{20}_4 0.9991. Found %: C 62.10, 61.98; H 8.24, 8.36; Si 11.20, 11.38. $C_{13}H_{21}SiNO_2$. Calculated %: C 62.15; H 8.37; Si 11.15. The residue amounted to 14.3 g.

SUMMARY

1. By the method of "competing" reactions relative reactivities were determined in the nitration of a series of aromatic sila-hydrocarbons in which the aromatic ring occupied various positions with respect to the silicon atom.

2. The results confirm the presence of conjugation between the Si–C bond and the aromatic ring in trialkylbenzylsilanes.

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CHEMISTRY OF 1,3-CYCLOHEXANEDIONE

COMMUNICATION 5. CHEMICAL PROPERTIES OF ENOL ETHERS OF 1,3-CYCLOHEXANEDIONE AND ITS DERIVATIVES

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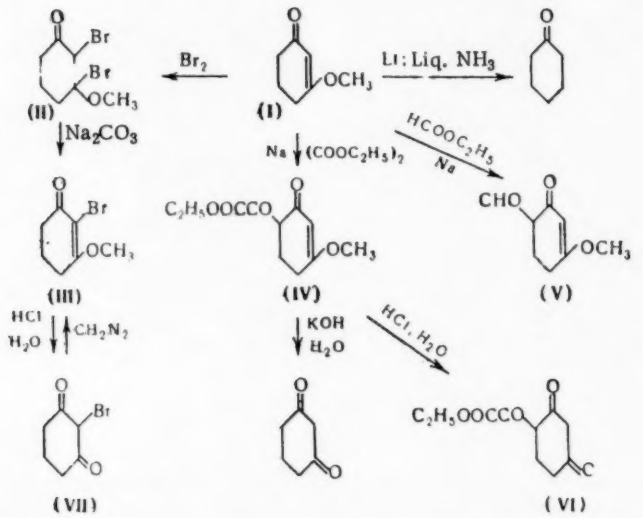
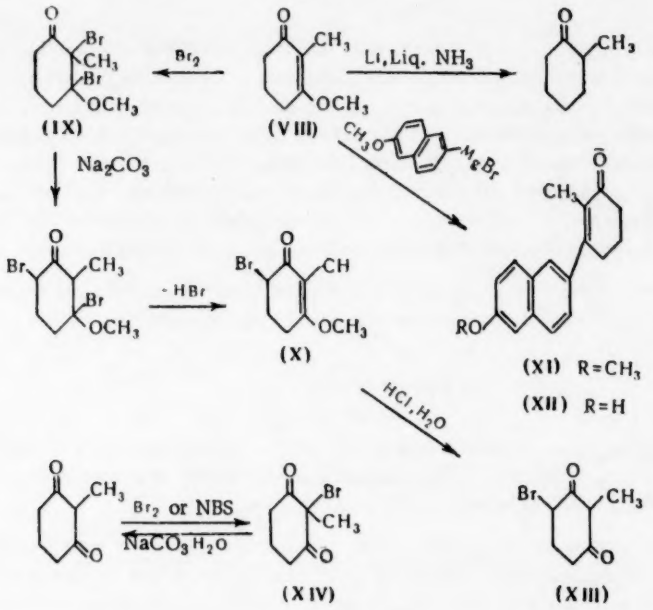
It is known that, under the action of diazomethane [1-3] or alcohols [4] in presence of an acid catalyst, 1,3-cyclohexanedione ("dihydroresorcinol") and its derivatives readily form enol ethers, which are liquids or low-melting solids sensitive to hydrolysis by acids and alkalis [3]. The enol ethers of 1,3-cyclohexanedione have recently found wide application in organic synthesis, in particular in the synthesis of steroids and their analogs [4-7].

It was of interest to make a more detailed study of the chemical properties of enol ethers of 1,3-cyclohexanedione (3-alkoxy-2-cyclohexen-1-ones), which have a peculiar combination of functional groups in a cyclic system.



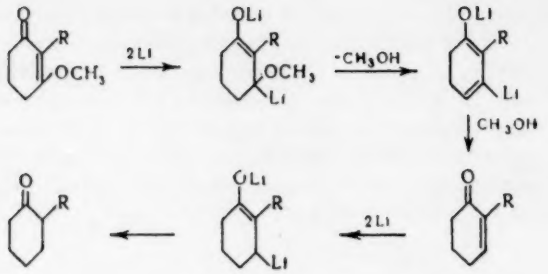
For an analysis of data in the literature, it may be concluded that the ketonic character of the carbonyl group in enol ethers of 1,3-cyclohexanedione (3-alkoxy 2-cyclohexen-1-ones) is less marked than in the usual

cyclic ketones. Thus, Finnish investigators did not succeed in preparing the 2,4-dinitrophenylhydrazone of 3-methoxy-2-methyl-2 cyclohexen-1-one (VIII) [3]. It was also noted previously that the reaction of 6-methoxy-2-naphthylmagnesium bromide with the enol ether (VIII) in an ether-benzene medium proceeds almost exclusively with the participation of the enol form of the ketone [6]. In confirmation of these results we have found that the enol ethers (I) and (VIII) do not give semicarbazones even after 24 hours' standing with semicarbazide in an alcoholic or aqueous medium. However, by carrying out the reaction of 6-methoxy-2-naphthylmagnesium bromide with the enol ether (VIII) in tetrahydrofuran [8] we were able to suppress to a considerable extent the enolization of the ketone (VIII) under the conditions of the Grignard synthesis and obtain, after hydrolysis with hydrochloric acid, the normal product (XI).



3-Methoxy-2-cyclohexen-1-one (I) readily adds one molecule of bromine in the cold with formation of an unstable oily dibromide (II), which loses hydrogen bromide under the action of aqueous sodium carbonate with formation of 2-bromo-3-methoxy-2-cyclohexen 1-one (III). In acid medium the latter is hydrolyzed to 2-bromo-1,3-cyclohexanedione (VII), which on treatment with diazomethane is converted back into the enol ether (III) [9]. On bromination, 3-methoxy-2-methyl-2-cyclohexen-1-one (VIII) also forms an oily dibromide (IX), which, however, on subsequent treatment with sodium carbonate and hydrochloric acid gives not 2-bromo-2-methyl-1,3-cyclohexanedione (XIV), but the isomeric bromo diketone (XIII). For the purpose of identification, the bromo diketone (XIV) was prepared by the bromination of 2-methyl-1,3-cyclohexanedione with bromine or N-bromosuccinimide. Thus, on elimination of hydrogen bromide from the dibromide (IX) a bromine atom migrates, and the resulting enol ether appears to have the structure (X). On standing, or when heated with aqueous sodium carbonate, 2-bromo-2-methyl-1,3-cyclohexanedione (XIV) is converted into 2-methyl-1,3-cyclohexanedione and other unidentified products.

Under the usual conditions the double bond of the enol ethers (I) and (VIII) was found to be passive to the action of such an active nucleophilic reagent as sodiomalonic ester. Moreover, the enol ethers (I) and (VIII) were not hydrogenated over palladium and platinum catalysts under normal conditions. On reduction with lithium in liquid ammonia the enol ethers (I) and (VIII) were respectively converted into cyclohexanone and 2-methylcyclohexane, probably via the intermediate stage of α,β-unsaturated ketones in accordance with the following scheme:



The methylene group in the 6-position of the enol ethers (I) and (VIII) was found to be incapable of undergoing the Michael reaction under the usual conditions (potassium t-butoxide in t-butyl alcohol). However, 3-methoxy 2-cyclohexen-1-one (I) reacts vigorously in the Claisen reaction with formic and oxalic esters with formation of the corresponding acyl derivatives (V) and (IV). Acid hydrolysis of the cyclohexeneglyoxylic ester (IV) gives the 2,4-dioxocyclohexane-1-glyoxylic ester (VI), which is converted into 1,3-cyclohexanedione when heated with aqueous alkali (hydrolysis with elimination of the oxalic residue). The methoxyoxocyclohexeneglyoxylic ester (IV) is a fairly stable compound, which is not decarboxylated even at high temperature (200-210°), probably because of the complete enolizability of the carbonyl group of the oxalic residue.

The cases of inertness in the enol ethers (I) and (VIII) noted in the present work for certain typical reactions may be explained by the vinylology of these compounds with aliphatic esters.

EXPERIMENTAL

The enol ethers of 1,3-cyclohexanedione and 2-methyl-1,3-cyclohexanedione (I) and (VIII) [b. p. 123-124° (19 mm) and 98-99° (3 mm), respectively] were prepared by the action of diazomethane on 1,3-cyclohexanedione [1] and on 2-methyl-1,3-cyclohexanedione [2] in ether solution.

Reaction of 6-Methoxy-2-naphthylmagnesium Bromide with 3-Methoxy-2-methyl-2-cyclohexen-1-one (VIII). A solution of 4.1 g of 3-methoxy-2-methyl-2-cyclohexen-1-one (VIII) in 10 ml of tetrahydrofuran was added to a stirred cooled (ice water) Grignard reagent prepared from 1.3 g of magnesium and 12.5 g of 2-bromo-6-methoxynaphthalene (m. p. 104-105°) in 45 ml of tetrahydrofuran. After 12 hours at room temperature the reaction mixture was decomposed with ice and dilute hydrochloric acid, heated to 50-60° for one hour, and extracted with ether. The ether solution was washed with dilute alkali, and after removal of solvent the residue was heated in a vacuum (1 mm) at a bath temperature of 165° to remove 2-methoxynaphthalene and other low-boiling products. The residual oil was dissolved in benzene and passed through an alumina column. We then obtained 3.4 g of the reaction product (XI), m. p. 96-97° (from hexane). Found %: C 80.76, 80.99; H 6.79, 6.80. $C_{18}H_{18}O_2$. Calculated %: C 81.17; H 6.81.

The 2,4-dinitrophenylhydrazone had m. p. 180-181° (from methanol). Found %: C 64.37, 64.36; H 5.00, 5.00; N 12.50, 12.34. $C_{24}H_{22}O_5N_4$. Calculated %: C 64.56; H 4.96; N 12.55.

A mixture of 0.6 g of this reaction product (XI) and 1.2 g of aluminum chloride was boiled in 10 ml of xylene for eight minutes. When cool, the reaction mixture was decomposed with dilute hydrochloric acid and extracted with ether. When the ether-xylene solution was washed with dilute caustic alkali there was a precipitate of the phenoxide, which gave 0.2 g of tricyclic phenol (XII), m. p. 165-166° (from aqueous methanol). Found %: C 80.73, 80.73; H 6.41, 6.42. $C_{17}H_{16}O_2$. Calculated %: C 80.90; H 6.35.

The 2,4-dinitrophenylhydrazone had m. p. 256-257° (decomp.). Found %: N 13.02, 13.18. $C_{23}H_{20}O_5N_4$. Calculated %: N 12.94.

Bromination of 3-Methoxy-2-cyclohexen-1-one (I). With cooling with ice water and stirring, 1.6 g of bromine in 10 ml of carbon tetrachloride was added to 1.2 g of 3-methoxy-2-cyclohexen-1-one in 10 ml of carbon tetrachloride. The dibromide (II) was then precipitated as a viscous oil, and was separated by decantation

from the solvent and vacuum-dried. Found %: Br 53.28, 54.12. $C_7H_{10}O_2Br_2$. Calculated %: Br 55.94.

A solution of the dibromide (II) in chloroform was shaken with excess of sodium carbonate powder and then washed with water. From the chloroform layer we isolated 2-bromo-3-methoxy-2-cyclohexen-1-one (III), 1.1g, m. p. 94-95°, undepressed by admixture of a known sample [9].

Bromination of 3-Methoxy-2-methyl-2-cyclohexen-1-one (VIII). In the bromination of 1.4 g of 3-methoxy-2-methyl-2-cyclohexen-1-one (VIII) and the decomposition of the resulting oily dibromide (IX) with sodium carbonate, as described above, we isolated 0.4 g of 6-bromo-3-methoxy-2-methyl-2-cyclohexen-1-one (X), m. p. 27-28° (from hexane). Found %: C 43.83, 43.82; H 4.93, 5.05; Br 36.51, 36.53. $C_8H_{11}O_2Br$. Calculated %: C 43.83; H 5.02; Br 36.53.

Hydrolysis of 6-Bromo-3-methoxy-2-methyl-2-cyclohexen-1-one (X). A mixture of 0.3 g of 6-bromo-3-methoxy-2-methyl-2-cyclohexen-1-one (X) and 5 ml of dilute (1:1) hydrochloric acid was left at room temperature for two days. The resulting crystalline product was filtered off and washed with ether. We obtained 0.12 g of 4-bromo-2-methyl-1,3-cyclohexanedione (XIII), m. p. 106-108° (decomp.). Found %: Br 38.66, 38.70. $C_7H_9O_2Br$. Calculated %: Br 39.02.

The substance was soluble in dilute sodium carbonate solution, and on standing or when heated it decomposed with liberation of hydrogen bromide.

Bromination of 2-Methyl-1,3-cyclohexanedione. 1. A mixture of 2.4 g of 2-methyl-1,3-cyclohexanedione and 3.6 g of N-bromosuccinimide in 20 ml of carbon tetrachloride was heated at 70-80° for 15 minutes. The solution was filtered and vacuum-evaporated to dryness. Distillation of the residue gave 2.4 g of 2-bromo-2-methyl-1,3-cyclohexanedione (XIV); b. p. 90-93° (3 mm), $n^{20}D$ 1.5215; m. p. 17-19°. Found %: Br 38.81, 38.74. $C_7H_9O_2Br$. Calculated %: Br 39.02.

2. In the bromination of 2.4 g of 2-methyl-1,3-cyclohexanedione in a mixture of 10 ml of water and 10 ml of chloroform by means of 4 g of bromine at room temperature we isolated 2 g of 2-bromo-2-methyl-1,3-cyclohexanedione (XIV).

Conversion of 2-Bromo-2-methyl-1,3-cyclohexanedione (XIV) into 2-Methyl-1,3-cyclohexanedione. 1. A mixture of 2 g of 2-bromo-2-methyl-1,3-cyclohexanedione (XIV) and 20 ml of 5% sodium carbonate solution was heated with stirring in a boiling water bath for 30 minutes. The cooled solution was filtered and then acidified with dilute hydrochloric acid. There was a precipitate of 0.7 g of 2-methyl-1,3-cyclohexanedione, m. p. 208-209°, undepressed by admixture of a known sample [10].

2. 2-Bromo-2-methyl-1,3-cyclohexanedione (XIV) (2.8 g) was kept for two days at room temperature. The substance gradually began to crystallize with liberation of hydrogen bromide. The solid product was washed with ether and recrystallized from water. We obtained 0.5 g of 2-methyl-1,3-cyclohexanedione, m. p. 208-209°.

Reduction of 3-Methoxy-2-cyclohexen-1-one with Lithium in Liquid Ammonia. A solution of 4 g of 3-methoxy-2-cyclohexen-1-one in 30 ml of ether was added to a solution of 0.6 g of lithium in 500 ml of liquid ammonia. After ten minutes the excess of lithium was decomposed with ammonium chloride and, after removal of ammonia, the residue was treated with hydrochloric acid and extracted with chloroform. Vacuum fractionation gave 1.2 g (39%) of cyclohexanone [b. p. 53-55° (20 mm), $n^{20}D$ 1.4500], the 2,4-dinitrophenylhydrazone of which (m. p. 158-159°) showed no depression of melting point in admixture with a known sample.

Reduction of 3-Methoxy-2-methyl-2-cyclohexen-1-one with Lithium in Liquid Ammonia. Reduction, as described above, of 6 g of 3-methoxy-2-methyl-2-cyclohexen-1-one with 1 g of lithium in liquid ammonia gave 1.4 g (29%) of 2-methylcyclohexanone [b. p. 106-108° (10 mm), $n^{20}D$ 1.4490], the semicarbazone of which (m. p. 189-191°) showed no depression of melting point in admixture with a known sample.

Reaction of 3-Methoxy-2-cyclohexen-1-one with Oxalic Ester in Presence of Sodium. In portions over a period of 10-15 minutes 0.5 g of sodium was added to a mixture of 2.5 g of 3-methoxy-2-cyclohexen-1-one (I) and 3 g of oxalic ester in 20 ml of benzene. After one hour the solution was treated with water, and the alkaline layer was acidified with acetic acid. The oil then precipitated was extracted with chloroform and vacuum-distilled. We obtained 2.5 g of reaction product, b. p. 188-192° (4 mm), from which we isolated 1.6 g (35%) of 4-methoxy-2-oxo-3-cyclohexene-1-glyoxylic ester (IV), m. p. 53-55° (from a mixture of isooctane and benzene). Found %: C 58.56, 58.69; H 6.13, 6.16. $C_{11}H_{14}O_5$. Calculated %: C 58.40; H 6.24.

4-Methoxy-2-oxo-3-cyclohexene-1-glyoxylic ester gives a dark coloration with ferric chloride, and under the action of 2,4-dinitrophenylhydrazine in methanol in presence of traces of hydrochloric acid it forms a pyrazole derivative, m. p. 202-203° (from methanol; λ_{max} 282 mμ (alcohol); light-yellow crystals which give no coloration with ferric chloride. Found %: N 14.87, 14.67. $C_{17}H_{16}O_7N_4$. Calculated %: N 14.95.

Hydrolysis of 4-Methoxy-2-oxo-3-cyclohexene-1-glyoxylic Ester (IV). 1. A mixture of 1 g of 4-methoxy-2-oxo-3-cyclohexene-1-glyoxylic ester (IV) and 10 ml of dilute (1:1) hydrochloric acid was heated for 10 minutes at 45-55°. When the mixture had cooled, the precipitate present was carefully crystallized from water. We obtained 0.65 g of 2,4-dioxocyclohexane-1-glyoxylic ester (VI), m. p. 130-131°. Found %: C 56.51, 56.71; H 5.67, 5.68. $C_{10}H_{12}O_5$. Calculated %: C 56.60; H 5.70.

2. A mixture of 0.4 g of 4-methoxy-2-oxo-3-cyclohexene-1-glyoxylic ester and 10 ml of 5% potassium hydroxide solution was heated to the boil, then cooled, acidified with hydrochloric acid, and extracted with chloroform. We obtained 0.06 g of 1,3-cyclohexanedione, m. p. 104-105°, undepressed by admixture of a known sample.

Reaction of 3-Methoxy-2-cyclohexen-1-one with Formic Ester in Presence of Sodium. Sodium (1 g) was added in portions over a period of 15-20 minutes to a mixture of 5 g of 3-methoxy-2-cyclohexen-1-one and 3 g of formic ester in 50 ml of ether. After 12 hours at room temperature the reaction mixture was treated with water, and the aqueous solution was acidified with acetic acid. The oil then precipitated was extracted with ether and vacuum-distilled. We obtained 2.8 g of a substance of b. p. 124-129° (3 mm) and $n^{20}D$ 1.5510. On standing in ether solution the substance crystallized. We then isolated 1 g of the formyl derivative, 4-methoxy-2-oxo-3-cyclohexene-1-carboxaldehyde (V), m. p. 76-78° (from ether). Found %: C 62.10, 62.17; H 6.59, 6.63. $C_9H_{10}O_3$. Calculated %: C 62.32; H 6.54.

The formyl derivative (V) gave a dark coloration with ferric chloride.

SUMMARY

1. Reaction of 6-methoxy-2-naphthylmagnesium bromide with the enol ether, 3-methoxy-2-methyl-2-cyclohexen-1-one (VIII), and subsequent hydrolysis with hydrochloric acid gave the tricyclic ketone (XI).

2. Bromination of 3-methoxy-2-cyclohexen-1-one (I) and 3-methoxy-2-methyl-2 cyclohexen-1-one (VIII) and subsequent treatment of the intermediate dibromides (II) and (IX) with aqueous sodium carbonate gave 2-bromo-3-methoxy-2-cyclohexen-1-one (III) and probably 6-bromo-3-methoxy-2-methyl-2-cyclohexen-1-one (X), respectively.

3. 3-Methoxy-2-cyclohexen-1-one (I) and 3-methoxy-2-methyl-2-cyclohexen-1-one (VIII) are reduced by lithium in liquid ammonia with formation of cyclohexanone and 2-methylcyclohexanone, respectively.

4. 3-Methoxy-2-cyclohexen-1-one (I) undergoes the Claisen reaction with formic and oxalic esters at the methylene group in the 6-position.

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POSSIBLE METHODS OF SYNTHESIZING SUBSTANCES ALLIED TO VITAMIN A*

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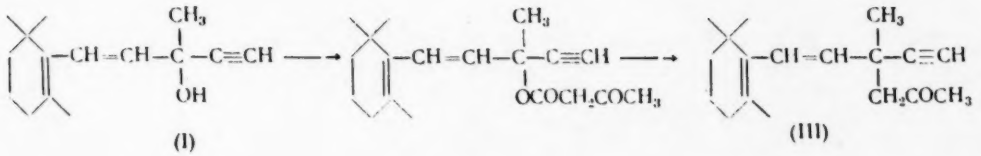
In the course of a systematic investigation of possible methods of synthesizing isoprenoids, we directed our attention to the readily accessible tertiary acetylenic alcohol 3-methyl-1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1-penten-4-yn-3-ol (C_{15} ynol (I)], which could be used in the synthesis of isoprenoid systems of the vitamin A type. With this object we first investigated the pyrolysis of the acetoacetate of the C_{15} ynol, in the hope of obtaining 6-methyl-8-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3,5,7-octatrien-2-one[C_{18} ketone (II)], an important intermediary on the route to the synthesis of vitamin A. It is known [1, 2] that the pyrolysis of acetoacetates of ethynylmethanols of the isoprenoid type usually leads to the corresponding isoprenoid dienones in good yields. It was found that the C_{15} ynol readily reacts with ketene dimer in ether solution in presence of small amounts of pyridine at from $-10°$ to $-15°$ with formation of the acetoacetate in high yield, and this, after the reaction mixture had been washed and dried and ether had been removed in a vacuum at room temperature, remained as a clear faintly yellowish oil, $n^{17.5}D$ 1.5185.

Unlike the acetoacetates of other acetylenic alcohols, which can be vacuum-distilled without decomposition and undergo pyrolysis only at 190-200°, the acetoacetate of the C_{15} ynol decomposes extremely readily when heated. When it is heated in a vacuum of about 0.05 mm, decomposition sets in at a bath temperature of only 80-90°; for this reason we did not succeed in isolating the acetoacetate of the C_{15} ynol in a purified state. After pyrolysis of 24 g of crude acetoacetate of the C_{15} ynol at 95-100° at 7 mm, with subsequent distillation, we obtained only 8 g of products, b. p. 120-130° (in the bath) at 0.05-0.02 mm and $n^{18.5}D$ 1.5742. By purification of the product with the aid of the Girard P reagent under the conditions for the isolation of the C_{18} ketone [3] we succeeded in isolating only 1 g of substance, from which by the usual method we obtained 0.8 g of semicarbazone, corresponding to the composition $C_{19}H_{29}ON_3$ and having a constant m. p. of 150.5-151° after three crystallizations from aqueous alcohol. This semicarbazone had λ_{max} (in alcohol) of 228.5 mμ. Hence, the ketone which we obtained by the pyrolysis of the acetoacetate of the C_{15} ynol under the conditions cited above was not the C_{18} ketone required. We are inclined to suppose, in accord with the results of Nazarov and Krasnaya [4], that the ketone that we obtained was probably the branched dienic ketone (III), formed by the pyrolysis of the acetoacetate of the C_{15} ynol without intramolecular rearrangement.



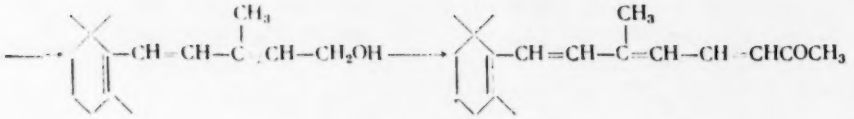
(I) (III)

* The work was carried out under the supervision of I. N. Nazarov.

The presence of acetylenic hydrogen in the ketone (III) is confirmed by the positive reaction given with an alcoholic-ammoniacal solution of silver nitrate.

With the object of utilizing a second possible method of passing from the C_{15} ynol to the C_{18} ketone (II) we examined the following scheme:

(I) (IV)

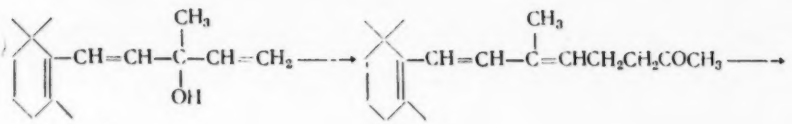


(II)

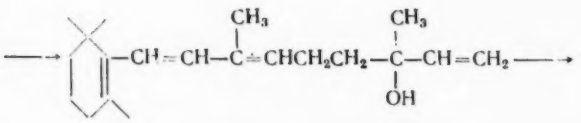
It was found that the hydrogenation of the C_{15} ynol (I) goes very smoothly in presence of 5% of palladium on calcium carbonate and leads to a high yield of 3-methyl-1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1,4-pentadien-3-ol (C_{15} dienol (IV)], which was known previously only as a 50% mixture [5]. We studied also another method of synthesizing the C_{15} dienol based on the Normant vinylation of β-ionone. Even under very mild conditions, however, the reaction was accompanied by much dehydration and gave the C_{15} dienol in a yield of about 40-45%. The two samples of C_{15} dienol (IV) prepared by these methods were found to be completely identical in properties. Unfortunately, we did not succeed in preparing any crystalline derivatives (p-nitrobenzoates, phenylurethanes) of this tertiary vinyl alcohol.

Attempts at the isomerization of the C_{15} dienol by the action of very dilute acids led to the formation either of resins or of a mixture of hydrocarbons. Attempts at isomerization by conversion of the C_{15} dienol into a bromo or chloro derivative by the action of phosphorus tribromide or trichloride and by treatment of this with potassium acetate in N,N-dimethylformamide with subsequent hydrolysis of the resulting acetate [6] again did not give satisfactory results. Hence, we did not succeed in carrying out this scheme for the synthesis of the C_{18} ketone either.

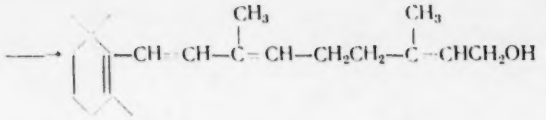
As the above-described experiments on the synthesis of the C_{18} ketone did not give satisfactory results, it was decided to attempt to pass from the C_{15} dienol (IV) to 6-methyl-8-(2,6,6-trimethyl-1-cyclohexen-1-yl)-5,7-octadien-2-one [C_{18}, 3,4-dihydro ketone (V)] and further to 4,5-dihydro vitamin A (VI) by the scheme:



(IV) (V)



(VII)



(VI)

There is a short mention in the literature of the synthesis of 4,5-dihydro vitamin A [7] by an analogous method, but no details are given, and there is no characterization of the product, apart from the absorption maximum.

We studied three methods for the synthesis of the C_{18} 3,4-dihydro ketone (V): 1) condensation of the bromo compound obtained from the C_{15} dienol with sodioacetoacetic ester with subsequent ketonic scission; 2) heating of the C_{15} dienol with acetoacetic ester; 3) pyrolysis of the acetoacetate of the C_{15} dienol. By the first method we obtained a yield of 60-65% of the C_{18} 3,4-dihydro ketone (V), identified as its semicarbazone, m. p. 160-161°. The second method led to the formation of much resin and a small amount of a complex mixture of unidentified products. The action of ketene dimer on an ether solution of C_{15} dienol in presence of pyridine at from − 15° to − 20° readily gave the acetoacetate of the C_{15} dienol, which, like the acetoacetate of the C_{15} ynol, underwent pyrolysis extremely readily: merely by heating at reduced pressure in a water bath. As a result of this reaction, from 18.5 g of the C_{15} dienol we obtained 10.5 g of product having b. p. 110-130° (in the bath) at 0.08-0.15 mm and $n^{13.5}D$ 1.5415, which was close in analysis to the C_{18} 3,4-dihydro ketone. However, the semicarbazone prepared after purification of the product with the aid of the Girard P reagent did not correspond to the semicarbazone of the C_{18} 3,4-dihydro ketone. Hence, again in the case of the pyrolysis of the acetoacetate of the C_{15} dienol the process appears to proceed differently from that occurring with acetoacetates of other tertiary vinyl methanols studied previously [1, 2]. We did not make a closer study of the structure of the ketone obtained.

By Normant vinylation the C_{18} 3,4-dihydro ketone (V) was converted in satisfactory yield into 3,7-dimethyl-9-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1,6,8-nonatrien-3-ol (VII). However, attempts to isomerize (VII) into 3,4-dihydro vitamin A by treatment with phosphorus tribromide and subsequent conversion of the bromo compound into the acetate by the action of potassium acetate in N,N-dimethylformamide and hydrolysis of the acetate were not successful. Apart from a large amount of resin, we obtained a small amount of a mixture of products not containing the hydroxy group, and the structure of these was not investigated more closely.

EXPERIMENTAL

3-Methyl-1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1-penten-4-yn-3-ol (I). This was prepared by a known method [8] by the action of lithium acetylide in liquid ammonia on β-ionone; yield 73%; b. p. 124-126° (2 mm); $n^{20}D$ 1.5080; λ_{max} (in alcohol) 235 mμ; found active H: 1.865; 1.971.

3-Methyl-1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1,4-pentadien-3-ol (IV). 1. Freshly distilled C_{15} ynol (104 g) was hydrogenated as a solution in 100 ml of alcohol in presence of 0.3 g of 5% $Pd/CaCO_3$ until the acetylene test was negative. At 750 mm and 21° 11.721 ml of hydrogen was absorbed (the theoretical amount was 11.699 ml). The mixture was filtered and solvent was distilled off. Vacuum fractionation gave 87 g (80%) of the C_{15} dienol; b. p. 113-115° (2 mm); $n^{20}D$ 1.5072; λ_{max} (in alcohol) 234.5 mμ (log ε 3.795); (in isooctane) 232 mμ (log ε 3.698). Found %: C 81.70, 81.91; H 10.89, 10.88. $C_{15}H_{24}O$. Calculated %: C 81.80; H 10.98. Found active hydrogen: 0.990; 0.897.

2. A solution of 19.2 g of β-ionone in 20 ml of dry ether was added over a period of 40 minutes to a suspension of vinylmagnesium bromide (from 26 g of vinyl bromide and 4.6 g of magnesium) in 60 ml of tetrahydrofuran and 60 ml of dry ether at from − 20° to − 22°. The cooling mixture was removed, and the mixture was stirred until the temperature rose to that of the room; it was left overnight. On the next day the mixture was heated for one hour at 35-40°, cooled, and poured into a mixture of ice and 20 g of ammonium chloride. The mixture was extracted three times with ether, and the ether extract was dried with magnesium sulfate. After removal of solvents under somewhat reduced pressure, the residue was fractionated at 2.5 mm. The fraction of

b. p. 115-117° (2.5 mm) was treated with an alcoholic solution of 0.1 mole of semicarbazide acetate, and on the next day was poured into water and extracted with petroleum ether. The organic layer was separated, dried with magnesium sulfate, and, after removal of solvent, vacuum-fractionated. We obtained 9 g (41%) of the C_{15} dienol; b. p. 112-114° (2 mm); $n^{20}D$ 1.5078. Found %: C 81.40, 81.40; H 10.77, 10.65. $C_{15}H_{24}O$. Calculated %: C 81.80; H 10.98. Found active hydrogen: 0.926; 1.10. λ_{max} (in alcohol) 234.5 mμ (log ε 3.793).

6-Methyl-8-(2,6,6-trimethyl-1-cyclohexen-1-yl)-5,7-octadien-2-one (V). To a solution of 44 g of the C_{15} dienol in 50 ml of dry ether 1 ml of pyridine was added; the mixture was cooled to from − 30° to − 20°, and a solution of 18 g of phosphorus tribromide in 20 ml of dry ether was added dropwise. The coolant was removed, and the mixture was stirred further for two hours. The mixture was poured into sodium bicarbonate solution, washed, and extracted with ether. The ether extract was dried with magnesium sulfate and filtered; ether was removed under reduced pressure at room temperature. The residue (47 g; $n^{20}D$ 1.5625; a heavy light colored oil) was added at from − 20° to − 25° over a period of 20 minutes to a suspension of sodio-acetoacetic ester in dry ether (4.6 g of sodium, 26 g of acetoacetic ester, 140 ml of absolute alcohol), the coolant was removed, and the mixture was stirred for two hours and left overnight. On the next day a solution of 20 g of sodium hydroxide in 130 ml of water was added to the mixture, which was stirred and heated in a water bath for four hours; it was then diluted with water and extracted with ether. The ether extract was dried with magnesium sulfate and filtered; ether was distilled off. The residue (45 g; $n^{21}D$ 1.5110) was boiled for three hours with 53 g of Girard P reagent in 554 ml of dry ether and 53 g of glacial acetic acid. The resulting solution was poured into a solution of 33 g of sodium hydroxide in 2 liters of water and washed with two 400 ml portions of ether. The aqueous layer was acidified with 150 ml of concentrated hydrochloric acid and carefully extracted with ether. The ether extract was washed with bicarbonate solution and then with water; it was dried with magnesium sulfate. After removal of ether the residue was vacuum-fractionated. We isolated 32 g (60%) of the C_{18} 3,4-dihydro ketone; b. p. 132-134° (0.5 mm); $n^{20}D$ 1.5218; semicarbazone, m. p. 160-161° (from mixture of benzene and petroleum ether), which corresponds to the literature [5]. Found %: C 82.82, 82.84; H 10.75, 10.79. $C_{18}H_{28}O$. Calculated %: C 83.05; H 10.84. λ_{max} (in isooctane): 240 mμ (log ε 4.219); 274.5 mμ (log ε 3.799).

3,7-Dimethyl-9-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1,6,8-nonatrien-3-ol (VII). A solution of 6.5 g of the C_{18} 3,4-dihydro ketone in 20 ml of dry ether was added over a period of 40 minutes to a suspension of vinylmagnesium bromide (from 6.5 g of vinyl bromide and 1.2 g of magnesium) in 30 ml of tetrahydrofuran and 40 ml of dry ether at − 70°. The mixture was stirred for one hour at − 70°, one hour at room temperature, and one hour at 40-50°; it was then left overnight. On the next day, it was poured into a mixture of ice and ammonium chloride and carefully extracted with ether. The ether extract was dried with magnesium sulfate, ether was distilled off, and the residue was treated with an alcoholic solution of 0.025 moles of semicarbazide acetate. On the next day the mixture was poured into water and extracted with petroleum ether. The extract was dried with magnesium sulfate and, after removal of solvent, fractionated. We obtained 3.7 g (50%) of product; b. p. 125-140° (in bath at 0.09 mm); $n^{19}D$ 1.5280. Found %: C 83.08, 82.96; H 11.07, 11.22. $C_{20}H_{32}O$. Calculated %: C 83.24; H 11.18. Found active hydrogen: 1.16; 1.05.

SUMMARY

1. By the hydrogenation of 3-methyl-1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1-penten-4-yn-3-ol and the Normant vinylation of β-ionone, 3-methyl-1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1,4-pentadien-3-ol was prepared.

2. Normant vinylation of the C_{18} 3,4 dihydro ketone gave 3,7-dimethyl-9-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1,6,8-nonatrien-3-ol.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

SYNTHESIS OF PYRIDINE BASES FROM 1-BUTEN-3-YNE

COMMUNICATION 3. CATALYTIC SYNTHESIS OF 6-t-BUTYL- AND 6-ARYL-2-PICOLINES

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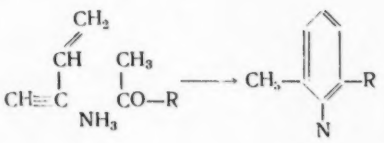
In previous papers [1] we described a new method for the synthesis of alkyl derivatives of pyridine by the catalytic condensation of dialkyl(3-buten-1-ynyl)methanols with ammonia and also of aliphatic ketones with 1-buten-3-yne and ammonia over heterogeneous catalysts in the vapor phase. In the present work, we studied the condensation of 2-phenyl-5-hexen-3-yn-2-ol with ammonia and also of acetophenone, 4'-methylacetophenone, 4'-ethylacetophenone, and pinacolone with 1-buten-3-yne and ammonia over $Cd_3(PO_4)_2/Al_2O_3$ at 400°. It was found that in the condensation both of 2-phenyl-5-hexen-3-yne and ammonia the main product was the same, 6-phenyl-2-picoline, but the yield was considerably higher in the second case than in the first.

The structure of 6-phenyl-2-picoline was proved by the identity of its principal constants with data in the literature, its oxidation to the known 6-phenylpicolinic acid, and the decarboxylation of the latter to 2-phenylpyridine, whose picrate had a melting point in accord with data in the literature. On introduction of 4'-methylacetophenone, 4'-ethylacetophenone, and pinacolone into the reaction with 1-buten-3-yne and ammonia we obtained, respectively, 6-p-tolyl-2-picoline, 6-p-ethylphenyl-2-picoline, and 6-t-butyl-2-picoline. In all the cases given in this work the main product, the 6-aryl(alkyl)-2-picoline, was accompanied by high-boiling bases, the structures of which we did not prove.

Our results are fully in accord with the reaction scheme given previously, according to which methyl ketones with a tertiary carbon atom or phenyl nucleus in the α-position to the carbonyl group should give only one reaction product with 1-buten-3-yne and ammonia:



in which R = $(CH_3)_3C$—; C_6H_5—; *p*-$CH_3C_6H_5$—; *p*-$C_2H_5C_6H_4$—. This scheme explains the negative result of the attempted catalytic reaction of benzophenone with 1-buten-3-yne and ammonia. It is interesting that under these conditions pyridine bases were not obtained from 4'-methoxyacetophenone.

EXPERIMENTAL

The synthesis of pyridine bases was carried out over 40 ml of $Cd_3(PO_4)_2/Al_2O_3$ (20:80) catalyst by the method given in the preceding paper [1]. The method of preparing the catalyst is described in the same place. 2-Phenyl-5-hexen-3-yn-2-ol [b. p. 102° (2.5 mm); m. p. 36°] was synthesized from acetophenone and 1-buten-3-yne [2] by Iotsich's method.

Catalytic Condensation of 2-Phenyl-5-hexen-3-yn-2-ol with Ammonia. 2-Phenyl-5-hexen-3-yn-2-ol (12 g) was passed over the catalyst at a space velocity of 1.3 hr^{-1} at 400°. The alcohol and ammonia were fed into the reaction space at a molar ratio of 1:3. The catalyzate, which collected in a trap cooled with ice water, was treated with hydrochloric acid (1:1) and washed with ether. The bases, which were liberated with potassium hydroxide, were dried and distilled from a Claisen flask; the following fractions were collected: Fraction I, b. p. up to 128° (6 mm), 0.1 g; Fraction II, b. p. 128-131° (6 mm), 1.7 g; residue 0.55 g. Refractionation of Fraction II gave 6-phenyl-2-picoline; b. p. 125-126° (5 mm); $n^{20}D$ 1.6057. Calculated MR 54.35; found MR 54.97.

Picrate, m. p. 141-142°. Found %: N 14.15, 14.25. $C_{18}H_{14}N_4O_7$. Calculated %: N 14.06. The literature [3] gives b. p. 97-100° (1.5 mm); picrate, m. p. 135°.

A study was made of the effect of reaction conditions at a molar ratio of alcohol to ammonia of 1:3 on the yield of 6-phenyl-2-picoline. The results are given in Table 1.

TABLE 1

Expt.	Rate of feed of alcohol (hr^{-1})	Reaction temp. (°C)	Yield of catalyzate (% on alcohol passed)	Yield of phenylpicoline (% on alcohol)
Effect of reaction temperature				
1	1,3	360	71,3	8,0
2	1,3	400	87,5	14,4
3	1,3	450	78,2	11,5
4	1,3	500	60,8	5,9
Effect of rate of feed of alcohol				
5	0,5	400	60,8	9,8
6	0,9	405	76,0	10,0
7	1,3	400	87,5	14,4
8	1,8	400	83,8	12,2

Catalytic Condensation of Acetophenone and 1-Buten-3-yne with Ammonia. A mixture of 41.6 g of acetophenone and 6 g of 1-buten-3-yne was passed over the catalyst at a rate of 1.4 hr^{-1} at 400° with molar proportions of 1-buten-3-yne, acetophenone, and ammonia of 1:3:6. We obtained 41.4 g of catalyzate, which was treated as indicated above. We separated 12.5 g of bases, which on distillation from a Claisen flask gave the following fractions: Fraction I, b. p. up to 128° (6 mm), 0.5 g; Fraction II, b. p. 128-131° (6 mm), 5.8 g; Fraction III, b. p. 200-210° (2 mm), 3.6 g; residue, 2.5 g. Fraction II consisted of 6-phenyl-2-picoline; after redistillation: b. p. 129-130° (6 mm); $n^{20}D$ 1.6055; d^{20}_4 1.0598. Picrate, m. p. 141-142°, undepressed by admixture of the picrate of 6-phenyl-2-picoline prepared from 2-phenyl-5-hexen-3-yn-2-ol. Of the neutral reaction products, fractionation gave 17.2 g of unchanged acetophenone.

A study was made of the effect of the conditions of the catalytic condensation of 1-buten-3-yne, acetophenone, and ammonia (rate of feed of mixture of acetophenone and 1-buten-3-yne 1.4 hr^{-1}) on the yield of 6-phenyl-2-picoline (Table 2).

TABLE 2

Expt.	Molar ratio* of 1-buten-3-yne: acetophenone	Reaction temp. (°C)	Yield of catalyzate (%)	Yield of 6-phenyl-2-picoline (% on 1-buten-3-yne)
		Effect of molar ratio of reactants		
1	1 : 1	400	81,0	24,9
2	1 : 2	400	94,8	28,1
3	1 : 3	400	97,9	30,0
4	1 : 4	400	96,5	34,8
5	1 : 5	400	95,4	23,8
		Effect of reaction temperature		
6	1 : 3	350	86,5	21,0
7	1 : 3	400	97,2	30,9
8	1 : 3	450	25,8	23,9

* Rate of feed of ammonia 30 liters/hr.

Oxidation of 6-phenyl-2-picoline. A mixture of 3.9 g of 6-phenyl-2-picoline, 150 ml of water, and 3.5 g of potassium permanganate was stirred and heated in a boiling water bath; after one hour a further 3.8 g of potassium permanganate was added, and stirring was continued at 100°. When the solution had been stirred in the water bath for 16 hours, it was decolorized. It was filtered from manganese dioxide, washed with ether, and evaporated to dryness; the residue was dissolved in 20 ml of water, and the solution was acidified to Congo Red with concentrated hydrochloric acid. The precipitate that formed was filtered off, washed twice with water, and recrystallized from water. The 6-phenylpicolinic acid obtained had m. p. 105° (the literature [4] gives m. p. 109°) and gave a red coloration with ferrous sulfate. The acid was heated up to 250° in Wood's metal and gave 2-phenylpyridine, identified as the picrate, m. p. 174-174.5°. The literature [5] gives m. p. 174°.

Condensation of 4'-Methylacetophenone with 1-Buten-3-yne and Ammonia. On passage of a mixture of 44.2 g of 4'-methylacetophenone and 8.6 g of 1-buten-3-yne over the catalyst at a space velocity of 1.4 hr^{-1} at 400° with molar proportions of 1-buten-3-yne, 4' methylacetophenone, and ammonia of 1:3:6 we obtained 18.3 g of bases, in the distillation of which we obtained the following fractions: Fraction I, b. p. up to 138° (3 mm), 1.1 g; Fraction II, b. p. 138-141° (3 mm), 10.0 g; Fraction III, b. p. 225-235° (3 mm), 4.2 g; residue 3.0 g. Fraction II consisted of 6-p-tolyl-2-picoline, and after two distillations it had: b. p. 139-140° (3 mm); m. p. 22°; $n^{20}D$ 1.6030; d^{20}_4 1.0372; found MR 59.57; calculated MR 58.97. Picrate, m. p. 151°. Found %: N 13.64, 13.72. $C_{19}H_{16}N_4O_7$. Calculated %: N 13.58. The yield of 6-p-tolyl-2-picoline was 30.2% (on the amount of 1-buten-3-yne taken). After three crystallizations from acetone Fraction III formed crystals of m. p. 164°. Found %: N 5.78, 5.63. From the neutral products we isolated 11.5 g of unchanged 4'-methylacetophenone.

Condensation of 4'-Ethylacetophenone with 1-Buten-3-yne and Ammonia. A mixture of 34.4 g of 4'-ethylacetophenone and 6 g of 1-buten-3-yne was passed together with ammonia into the catalysis tube at a space velocity of 1.4 hr^{-1} at 400° with molar proportions of 1-buten-3-yne, 4'-ethylacetophenone, and ammonia of 1:3:6. After the usual treatment of the catalyzate we obtained 11.9 g of bases. Fractionation gave: Fraction I, b. p. 173° (7 mm), 0.5 g; Fraction II, b. p. 173-185° (7 mm), 7.150 g; Fraction III, b. p. 200-215° (7 mm), 2.850 g; residue 1.4 g. Fraction II consisted of 6-p-ethylphenyl-2-picoline, which after redistillation had: b. p. 145-146° (2 mm); $n^{20}D$ 1.5812; d^{20}_4 1.0085; found MR 65.12; calculated MR 63.59.

Picrate: m. p. 146-147°. Found %: N 13.04, 13.26. $C_{20}H_{18}N_4O_7$. Calculated %: N 13.14. The yield of 6-p-ethylphenyl-2-picoline was 22.7%. By distillation of the neutral products we isolated 9.2 g of unchanged 4'-ethylacetophenone.

Condensation of Pinacolone with 1-Buten-3-yne and Ammonia. On passage of a mixture of 27.0 g of pinacolone and 5.5 g of 1-buten-3-yne together with ammonia over the catalyst at 350° with molar proportions of 1-buten-3-yne, pinacolone, and ammonia of 1:2:6 we obtained 23.5 g of catalyzate, from which we isolated

7.4 g of bases and 7.2 g of pinacolone. By reaction under similar conditions, we accumulated 82.5 g of bases, which were fractionated through a column of 25-plate efficiency and gave the following fractions: Fraction I, b. p. 130-156° (735 mm), 8 g; Fraction II, b. p. 174-180° (735 mm), 45.6 g; Fraction III, b. p. 195-207° (735 mm), 21.9 g; residue, 7.0 g. Fraction II consisted of 6-t-butyl-2-picoline, and after redistillation it had: b. p. 174° (730 mm); 72-73° (20 mm); $n^{20}D$ 1.4850; d^{20}_4 0.8913; found MR 47.93; calculated MR 48.719. Found %: N 14.67, 14.96. $C_{16}H_{18}N_4O_7$. Calculated %: N 14.81. Picrate, m. p. 158.5-159°.

The literature [5] gives b. p. 179° (760 mm). A study was made of the effect of reaction temperature and molar ratio of reactants on the yield of pyridine bases; the results are given in Table 3.

TABLE 3

Expt.	Molar ratio of 1-buten-3-yne: pinacolone	Reaction temp. (°C)	Yield of catalyzate (%)	Yield of 6-t-butyl-2-pinacoline (%)	Recovered pinacolone (% on amt. taken for reaction)
		Effect of molar ratio of reactants			
1	1 : 1	400	69,0	21,6	10,1
2	1 : 2	400	75,5	26,3	16,8
3	1 : 3	400	76,8	25,9	20,3
4	1 : 4	400	81,2	26,2	25,8
		Effect of reaction temperature			
5	1 : 2	300	90,3	19,1	43,6
6	1 : 2	350	85,4	29,0	32,6
7	1 : 2	400	75,5	26,5	16,8
8	1 : 2	450	70,5	11,8	14,4

Catalytic Treatment of Acetophenone, 4'-Methylacetophenone, 4'-Ethylacetophenone, and Pinacolone with Ammonia. These experiments were again carried out over $Cd_3(PO_4)_2/Al_2O_3$ at 400°. The molar ratio of ketone to ammonia was 1:2. The space velocity for the feed of ketone was 1.4 hr^{-1}. The catalyzates obtained were treated as in the previous cases. Not with any of the ketones were bases obtained.

SUMMARY

1. By the catalytic condensation of 2-phenyl-5-hexen-3-yn-2-ol with ammonia, and also that of acetophenone with 1-buten-3-yne and ammonia, over a $Cd_3(PO_4)_2/Al_2O_3$ catalyst at 400°, 6-phenyl-2-picoline was obtained.

2. By the analogous reactions of 4'-methylacetophenone, 4'-ethylacetophenone, and pinacolone with 1-buten-3-yne and ammonia, 6-p-tolyl-, 6-p-ethylphenyl-, and 6-t-butyl-2-picolines were obtained.

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SYNTHESIS AND PROPERTIES OF DI- AND TRI-PHENYLALKANES AND THEIR HYDROGENATION PRODUCTS OF COMPOSITION $C_{23} - C_{27}$

COMMUNICATION 3. SELECTIVE HYDROGENATION OF SOME ALKYLTRIPHENYLMETHANES

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In previous work [1] we prepared some alkyldicyclohexylphenylmethanes $(C_6H_{11})_2(C_6H_5)CR$, where R = C_4, iso-C_4, C_6, and $-\underset{\underset{C_2}{|}}{C}-(C)_4$, by incomplete hydrogenation of the corresponding alkyltriphenylmethanes.

In the present work we continued this investigation and have prepared $(C_6H_{11})_2(C_6H_5)C(C)_7$ and $(C_6H_{11})_2(C_6H_5)-\underset{\underset{C}{|}}{C}-C(C)_6$ by the selective hydrogenation of the corresponding alkyltriphenylmethanes. We prepared also 4-cyclohexyl-1,7-diphenylheptane and 4-hexyl-1,7-diphenylheptane by organomagnesium synthesis. The properties of these hydrocarbons are shown in Tables 1 and 2. Of hydrocarbons of types $(C_6H_{11})_2(C_6H_5)CR$ and $(C_6H_5)_2(C_6H_{11})CR$, only the incomplete-hydrogenation products of triphenylmethane itself have been described in the literature: $(C_6H_{11})_2(C_6H_5)CH$, prepared by Godchot [2] by the hydrogenation of $(C_6H_5)_3CH$ over Ni at 220° [b. p. 210-212° (20 mm); d^{13}_4 0.9894] and $(C_6H_{11})(C_6H_5)_2CH$, prepared by Neunhoeffer [3] by the hydrogenation of $(C_6H_5)_3CH$ over platinum oxide at room temperature (m. p. 56°).

In the present investigation we continued experiments on the selective hydrogenation of alkyltriphenylmethanes under conditions of lower temperatures. We carried out the incomplete hydrogenation of alkyltriphenylmethanes $(C_6H_5)_3CR$, where R = C_4, iso-C_4, and C_6, both at 100° in presence of Raney nickel and at 180° in presence of Bag's catalyst under pressure. The hydrogenation products, consisting of mixtures of hydrocarbons differing in degree of hydrogenation, were separated in a chromatographic column of ASM grade silica gel. Conditions were first selected that permitted the separation of artificially compounded mixtures of tricyclohexyl- and triphenyl-alkanes. The results of the chromatographic separation of the above hydrogenation products showed that lowering of the hydrogenation temperature does not permit the formation of hydrocarbons of type $(C_6H_5)_2(C_6H_{11})CR$. Apart from unchanged alkyltriphenylmethanes (up to 60%), the hydrogenation products consisted of small amounts of alkyldicyclohexylphenylmethanes (up to 20%) and alkyltricyclohexylmethanes (up to 10%); alkylcyclohexyldiphenylmethanes were absent. On the basis of our results we consider the mechanism of the hydrogenation of alkyltriphenylmethanes to alkyltricyclohexylmethanes over nickel catalysts to be as follows:

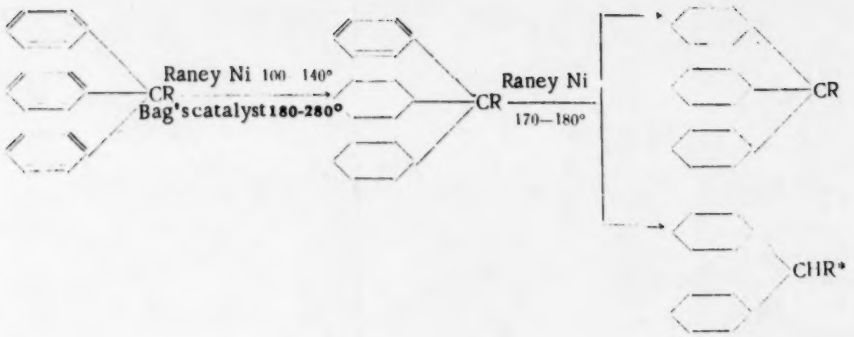
TABLE 1

Hydrocarbon	B. p. in °C (p in mm)	F.p. (°C)	d_4^{20}	n_D^{20}	MR found	MR calculated	Found (%) C	Found (%) H	Calculated % C	Calculated % H	Viscosity (centistokes) 20°	50°	100°	150°
$C_6H_5-C\equiv C-C\equiv C-C(C_6H_{13})(C_{25}H_{26})-C\equiv C-C_6H_5$	143—145(0,5)	—60	0,9148	1,5120	110,34	110,45	88,90 88,99	11,13 11,17	89,20	10,80	31,89	9,88	3,21	1,65
$C_6H_5-C\equiv C-C\equiv C-C(C_6H_{11})(C_{25}H_{24})-C\equiv C-C_6H_5$	182—185(1)	—10	0,9705	0,5419	108,40	108,25	90,01 89,92	10,20 10,11	89,74	10,26	967,79	51,40	5,24	3,08
$C_6H_5-C\equiv C-C\equiv C-C(C_6H_5)-C\equiv C-C_6H_5$ [4]	205—206(0,5)	—15	1,0013	1,5650							97,85	20,50	5,49	1,65

TABLE 2

Hydrocarbon	F.p. (°C)	Before chromatography d_4^{40}	Before chromatography n_D^{40}	After chromatography d_4^{40}	After chromatography n_D^{40}	MR found	MR calculated	Found (%) C	Found (%) H	Calculated (%) C	Calculated (%) H
$(C_6H_{11})_2(C_6H_5)C-C\equiv C-C\equiv C-C^*$ [1] $C_{23}H_{26}$	0	0,9700	1,5390	0,9631	1,5380	101,46	100,40	89,30 89,28	10,84 10,84	88,44	11,56
$(C_6H_{11})_2(C_6H_5)C-C\equiv C-C^*(C)=C$ [1] $C_{23}H_{24}$	—2	0,9714	1,5370	0,9601	1,5320	100,39	100,40	88,74 88,96	11,34 11,53	88,44	11,56
$(C_6H_{11})_2(C_6H_5)C(C)_4{}^*$ [1] $C_{25}H_{40}$	—2	0,9458	1,5200	0,9513	1,5230	109,30	109,65	87,97 88,05	11,84 11,85	88,15	11,85
$(C_6H_{11})_2(C_6H_5)C(C)_7$ $C_{28}H_{42}$	15	0,9538	1,5230	0,9547	1,5250	113,50	114,30	87,87 88,07	11,86 11,88	88,04	11,97*
$(C_6H_{11})_2(C_6H_5)C-C(C)_6$ $C_{27}H_{44}$	34	0,9577	1,5265	0,9630	1,5320	118,68	118,85	88,66 88,67	11,11 11,10	87,95	12,05

* Viscosity at 50°, 530 centistokes; at 100°, 231 centistokes; at 150°, 5.03 centistokes.



The rate of hydrogenation does not appear to be the same for all three phenyl rings in alkyltriphenylmethanes. The first two phenyl rings are hydrogenated more rapidly and at a lower temperature. The third ring is hydrogenated more slowly, and it can be hydrogenated completely only at a higher temperature.

The formation of hydrocarbons of the series $(C_6H_{11})_2(C_6H_5)CR$ by the selective hydrogenation of alkyltriphenylmethanes (under optimum conditions, i.e., at 140° in presence of Raney nickel and at 270° in presence of Bag's catalyst, the hydrocarbons are obtained in 50% yield) is also of preparative interest. Actually the preparation of hydrocarbons of this series by the organomagnesium synthesis, i.e.,

$$(C_6H_{11})_2(C_6H_5)CX + RMgX \longrightarrow (C_6H_{11})_2(C_6H_5)CR + MgX_2$$

is rendered difficult by the instability of such halogen compounds [5] and their tendency to undergo elimination of HX and pass into $(C_6H_{11})(C_6H_5)C=$. The latter undergoes isomerization into (C_6H_{11})-$(C_6H_5)C-$. The synthesis of 4-cyclohexyl-1,7-diphenylheptane and 4-hexyl-1,7-diphenylheptane permitted us to compare the properties of these hydrocarbons with those of 1,4,7-triphenylheptane, which we had synthesized previously. Hence, we were able to determine the change in the properties of a triphenylalkane with noncentralized rings on replacement of one of the phenyl rings by a hexyl or cyclohexyl group (Table 1). The replacement of 4-phenyl by cyclohexyl leads to a small rise in freezing point, and replacement by hexyl leads to a sharp fall in freezing point (to − 60°).

EXPERIMENTAL**

4-Hexyl-1,7-diphenylheptane. From 145 g (0.73 mole) of (3-bromopropyl)benzene, 18 g (0.75 mole) of magnesium, and 57 g (0.36 mole) of ethyl heptanoate we obtained 63 g (50%) of a product of b. p. 225-235° (5 mm), which consisted of a mixture of 4-hexyl-1,7-diphenyl-4-heptanol and its dehydration products. After several distillations we isolated an alcohol having b. p. 241° (5 mm); d^{20}_4 1.9599; $n^{20}D$ 1.5260; found MR 112.69. $C_{25}H_{36}O$. Calculated MR 111.97. Found %: C 85.81; H 10.50; OH 4.83. Calculated %: C 85.13; H 10.33; OH 4.54. This alcohol was dehydrated by Ziegler's method [6], and from 42.5 g we obtained 17 g (43%) of a mixture of olefins; b. p. 205-206° (1 mm); d^{20}_4 0.9306; $n^{20}D$ 1.5250; found MR 110.10. $C_{25}H_{34}$. Calculated MR 109.98. On hydrogenation of 17 g of the mixture of olefins at 40° in presence of Raney nickel and hydrogen under pressure we obtained 11 g (65%) of 4-hexyl-1,7-diphenylheptane (Table 1).

* In the preceding investigation [1] it is shown that hydrogenation is accompanied by partial elimination of one of the rings with formation of $(C_6H_{11})_2CHR$.

** Laboratory worker V. P. Krukhtanova participated in the experimental work.

4-Cyclohexyl-1,7-diphenylheptane. From 120 g (0.6 mole) of (3-bromopropyl)benzene, 14.5 g (0.6 mole) of magnesium, and 51 g (0.32 mole) of ethyl cyclohexanecarboxylate we obtained 50 g (45%) of a mixture of 4-cyclohexyl-1,7-diphenyl-4-heptanol and its dehydration products. On dehydration by Ziegler's method [6] 50 g of the mixture gave 25 g of olefins; b. p. 193-194° (1 mm); $n^{20}D$ 1.5460. On hydrogenation of 21.5 g of the mixture of olefins under the conditions indicated above we obtained 14 g (65%) of 4-cyclohexyl-1,7-diphenylheptane (Table 1).

Dicyclohexyl(1-methylheptyl)phenylmethane. (1-Methylheptyl)triphenylmethane [7] (14 g) was hydrogenated at 140° in presence of 4 g of Raney nickel and hydrogen under pressure until hydrogen ceased to be absorbed. We obtained 10 g of hydrogenation product, which gave two fractions when distilled under reduced pressure: Fraction I, b. p. up to 175° (2 mm) and $n^{40}D$ 1.5130, 5 g; Fraction II, b. p. 175° (2 mm), d^{40}_4 0.9577, and $n^{40}D$ 1.5265, 4.5 g. The experiment was repeated, and we obtained 8.5 g of Fraction II. Before the hydrogenation product was subjected to chromatography, the conditions were found for the separation of artificially compounded mixtures of triphenyl- and tricyclohexyl-alkanes.

A mixture of 1 g of $(C_6H_5)_3C(C)_6$ ($n^{70}D$ 1.5655) and 1 g of $(C_6H_{11})_3C{-}C{-}C\begin{matrix}C\\C\end{matrix}$ ($n^{50}D$ 1.4972)

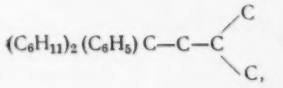
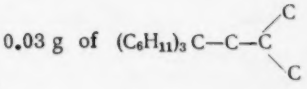
was passed in hexane solution through a column of 150 g of silica gel (height of lower part 56.5 cm, diameter 1.0 cm; height of upper part 42.0 cm, diameter 2.2 cm). Elution was carried out first with hexane, and then with benzene and ethanol. We obtained 0.75 g of $(C_6H_{11})_3C{-}C{-}C\begin{matrix}C\\C\end{matrix}$ ($n^{40}D$ 1.5010) and 0.68 g of $(C_6H_5)_3C(C)_6$ ($n^{70}D$ 1.5610). A mixture of 2 g of $(C_6H_5)_2C(C)_6$ ($n^{20}D$ 1.5390) and 2 g of $(C_6H_{11}C{-}C{-}C)_2{-}C{-}C{-}C_6H_{11}$ ($n^{20}D$ 1.4910) in hexane was subjected to chromatography under the same conditions. We obtained 1.66 g of $(C_6H_{11}{-}C{-}C{-}C)_2{-}C{-}C{-}C_6H_{11}$ ($n^{20}D$ 1.5040) and 1.5 g of $(C_6H_5)_2C(C)_6$ ($n^{20}D$ 1.5365). Under the same conditions 8.5 g of Fraction II of the hydrogenation product from $(C_6H_5)_3{-}\underset{\displaystyle C}{\underset{|}{C}}{-}(C)_6$ was subjected to chromatography, and as a result we obtained 6.16 g of $(C_6H_{11})_2(C_6H_5){-}\underset{\displaystyle C}{\underset{|}{C}}(C)_6$ (see Table 2) and 0.7 g of $(C_6H_{11})_3C{-}\underset{\displaystyle C}{\underset{|}{C}}(C)_6$ ($n^{40}D$ 1.5080). From 5.76 g of $(C_6H_{11})_2(C_6H_5){-}\underset{\displaystyle C}{\underset{|}{C}}(C)_6$ 41 g of HNO_3 (60%), and 70 g of H_2SO_4 (conc.), under the conditions stated by Hantzsch et al. [8], we obtained a nitro compound. Found %: C 79.24; H 9.47; N 4.28. $(C_6H_{11})_2(C_6H_4NO_2)C{-}\underset{\displaystyle C}{\underset{|}{C}}(C)_6$, Calculated %: C 78.38; H 10.50; N 3.39.

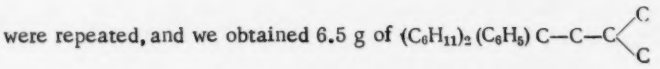
Dicyclohexylheptylphenylmethane. Heptyltriphenylmethane [7] (9 g) was subjected to incomplete hydrogenation at 140-150° in presence of Raney nickel (2 g) and hydrogen under pressure until hydrogen ceased to be absorbed. The hydrogenation product (7 g) was distilled under reduced pressure, and we isolated 4 g (about 50%) of a product having b. p. 180-181° (4 mm), d^{40}_4 0.9538; $n^{20}D$ 1.5230. Of this 3 g was subjected to chromatography and we obtained 2 g of $(C_6H_{11})_2(C_6H_5)C(C)_7$ (Table 2).

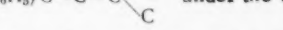
Heptyltriphenylmethane (18 g) was hydrogenated in presence of 5 g of Bag's catalyst at 180° under a pressure of hydrogen until absorption stopped. The hydrogenation product (17 g) was distilled under reduced pressure, and we obtained three fractions: Fraction I, b. p. up to 197° (3 mm), 2 g; Fraction II, b. p. 197-203° (3 mm), d^{40}_4 0.9625, and $n^{40}D$ 1.5360; Fraction III, b. p. 203° (3 mm), d^{40}_4 0.9750 and $n^{40}D$ 1.5470. The total amount of Fractions II and III was 14 g.

Fraction III (6 g) was subjected to chromatography, and we obtained 5.15 g of products: 1.19 g (23%) of $(C_6H_{11})_3C(C)_6$; 1.85 g (36%) of $(C_6H_{11})_2(C_6H_5)C(C)_6$; 0.75 g of intermediate fraction ($n^{40}D$ 1.5530-1.5690); and 1.32 g (41%) of $(C_6H_5)_3C(C)_6$. When the chromatography of $(C_6H_{11})_2(C_6H_5)C(C)_6$ was repeated, its refractive index did not change. Repeated chromatography of the intermediate fraction gave two products: a) $n^{40}D$ 1.5270 and b) $n^{40}D$ 1.5590.

Isobutyltriphenylmethane (167 g) was hydrogenated at 100° in presence of 25 g of Raney nickel and hydrogen under pressure until absorption stopped; 160 g of the hydrogenation product was distilled under reduced pressure. We obtained the following fractions: Fraction I, b. p. up to 153° (5 mm), $n^{40}D$ 1.5150, 18 g; Fraction II, b. p. 153-155° (1.5 mm), d^{40}_4 0.9687 and $n^{40}D$ 1.5365, 20 g; Fraction III, b. p. 168° (5 mm), d^{40}_4 0.9718, and $n^{40}D$ 1.5370, 20 g; Fraction IV, b. p. 168-175° (5 mm) and $n^{40}D$ 1.5610, 92 g. The yield of Fractions II and III was 24%, and 2.5 g of this mixture was subjected to chromatography. We obtained

1.7 g (68%) of  0.03 g of  and 0.4 g of an intermediate

fraction with $n^{40}D$ 1.5440. The experiments were repeated, and we obtained 6.5 g of 

and 1.5 g of an intermediate fraction. The latter (1.5 g) was again subjected to chromatography, and as a result we obtained 0.96 g of product having $n^{40}D$ 1.5340 and traces of a product having $n^{40}D$ 1.5900. From 5 g of  under the conditions stated above we obtained a nitro compound, m. p. 101-102° (from chloroform and benzene). Found %: C 75.06; H 8.92; N 4.05. $(C_6H_{11})_2(C_6H_4NO_2)CH$. Calculated %: C 75.67; H 9.06; N 4.65.

Butyltriphenylmethane (20 g) was hydrogenated at 200° in presence of Bag's catalyst (6g) and hydrogen under pressure until absorption ceased. The hydrogenation product (18 g) was distilled under reduced pressure, and we obtained the following fractions: Fraction I, b. p. 178° (2 mm), 3 g; Fraction II, b. p. 178-183° (2 mm), d 1.0035, and $n^{40}D$ 1.5670, 5 g; Fraction III, b. p. 183-191° (2 mm), d^{40}_4 1.0116, and $n^{40}D$ 1.5670, 8 g. Fraction III was subjected to chromatography and we obtained 7 g of product, of which 0.14 g (2%) was $(C_6H_{11})_3C(C)_4$; 1.63 g (23%) was $(C_6H_{11})_2(C_6H_5)C(C)_4$; ($n^{40}D$ 1.5300), and 5.25 g (75%) was $(C_6H_5)_3C(C)_4$; ($n^{40}D$ 1.5700). The constants of $(C_6H_{11})_2(C_6H_5)C(C)_4$ which had been retreated chromatographically are presented in Table 2. The hydrocarbon was nitrated under the conditions stated above. Found %: N 3.38. $(C_6H_{11})_2(C_6H_4NO_2)C(C)_4$ Calculated %: N 3.92.

SUMMARY

1. 4-Hexyl-1,7-diphenylheptane, 4-cyclohexyl-1,7-diphenylheptane, 1,1-dicyclohexyl-1-phenylheptane, and 1,1-dicyclohexyl-2-methyl-1-phenyloctane were prepared for the first time. The freezing points and viscosity properties of these hydrocarbons were determined.

2. In the hydrogenation of alkyltriphenylmethanes over nickel catalysts the following are formed: alkyldicyclohexylphenylmethanes and alkyltricyclohexylmethanes, which may be separated by fractional distillation and chromatography.

3. The selective hydrogenation of alkyltriphenylmethanes into hydrocarbons of the series $(C_6H_{11})_2(C_6H_5)CR$ may be carried out, under optimum conditions, in yields of up to 50%, which makes this method interesting from the preparative point of view.

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CATALYTIC SYNTHESIS OF NITRILES

COMMUNICATION 3. PREPARATION OF AROMATIC NITRILES

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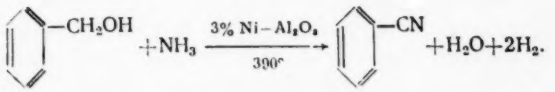
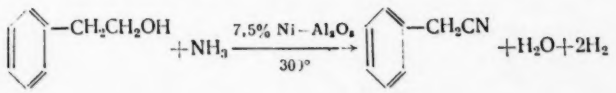
Aromatic nitriles have been prepared catalytically from various starting materials. Mitchell and Reid [1] prepared benzonitrile and hydrocinnamonitrile by passage of the vapors of the corresponding acids together with ammonia over silica gel at 500°. For the reaction between aromatic hydrocarbons and ammonia Coldwell and Chapman [2] proposed the use of molybdenum or tungsten oxides at 455-675°. Ritter and Schmidt [3] obtained up to 80% of benzonitrile from phthalic anhydride and ammonia in presence of alumina at 500°. Willett and Pailtrop [4] recommended the use of aluminum, nickel, or silicon oxide in the synthesis of nitriles from aromatic compounds halogenated in the nucleus and hydrocyanic acid. Reilly [5] took out a patent for the preparation of aromatic nitriles from N-alkyl aromatic amines and nitric oxide in presence of silica gel carrying a silver deposit at 450-550°. To avoid explosions the nitric oxide was diluted with pure nitrogen. The yield of nitrile did not exceed 23%. Keever and Nemec [6] synthesized benzonitrile in yields of up to 96% by the passage of benzoic acid vapor and ammonia over molybdenum oxide at 200-250°.

In previous communications [7] we have shown that primary aliphatic alcohols are converted into nitriles under the action of ammonia in presence of a nickel-alumina catalyst at 270-330°. It was shown that the yield of nitriles depends on the number of carbon atoms in the molecule of the alcohol. The object of the present work was the determination of optimum conditions for the synthesis of nitriles from aromatic alcohols and ammonia in presence of a nickel-alumina catalyst and the determination of the effect of the phenyl group on the composition of the reaction products. For the experiments we took benzyl alcohol, phenethyl alcohol, and 3-phenyl-1-propanol. The reaction was carried out at ordinary pressure at 270-330° in presence of catalysts containing 3, 7.5, and 15% of reduced nickel deposited on alumina.

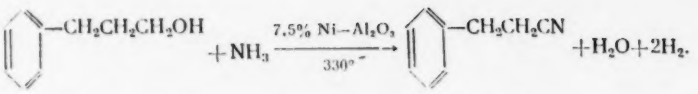
The results of a systematic investigation showed that in the action of ammonia on benzyl alcohol in a flow system at 390° in presence of a 3% nickel-alumina catalyst benzonitrile is formed in 51.7% yield:



The action of ammonia on phenethyl alcohol at 300° and on 3-phenyl-1-propanol at 330° in presence of a 7.5% nickel-alumina catalyst again gives the corresponding nitriles: phenylacetonitrile in 44.8% yield



and hydrocinnamonitrile in 50.8% yield.



We consider that these conditions for the synthesis of the nitriles are the optimum ones. Under the conditions used it was not found possible to detect a possible intermediate stage of amide formation.

EXPERIMENTAL

The physical constants of the original aromatic alcohols are presented in Table 1.

TABLE 1

Properties of Alcohols Taken for Investigation

Alcohol	Our preparations			Data in literature			Literature reference
	b.p. in °C (p in mm)	d_4^{20}	n_D^{20}	b.p. (°C)	sp. gr.	refractive index	
Benzyl alcohol	204 (748)	1,0491	1,5405	205,4—205,7	1,0498	1,5403	[8,9]
Phenethyl alcohol	218—219 (749)	1,0218	1,5355	219—221	1,0234	1,53574	[10]
3-Phenyl-1-propanol	232—233 (747)	1,0078	1,5335	235	1,0079	1,53565	[11,12]

The conditions used in the preparation of the catalysts and the experimental apparatus are described in a previous communication [7]. In all experiments the molar ratio of ammonia to alcohol was about 2, the space velocity for the passage of alcohol was 0.2 hr^{-1}, and the apparent volume of catalyst was 65 ml. In the catalyzates, which were dried with sodium sulfate, the nitrile content was determined by hydrolysis of a test sample with 50% sulfuric acid. The aromatic acid then formed was extracted with chloroform, solvent was distilled off, and the residue was treated with 0.5 N NaOH; excess of the latter was back-titrated with hydrochloric acid. The catalyzate from control experiments carried out under optimum conditions served for the isolation of the components and their characterization.

Table 2 gives the results of experiments on nitrile formation from benzyl alcohol. In accordance with the amount of catalyzate collected and its benzonitrile content, the optimum conditions for nitrile formation from this alcohol must be taken to be a temperature of 390° and the presence of a catalyst containing 3% of nickel on active alumina. Under these conditions we carried out a control experiment of five hours' duration. The catalyzate was collected in portions after each hour. The nitrile content was determined on the first, third, and fifth portions, and also on the combined catalyzate.

For the investigation of composition we took 41.5 g of dry catalyzate; in the first place we isolated 0.5 g of amines. The chloroplatinate prepared from these contained 22.62% of platinum. The platinum contents of the chloroplatinates from primary, secondary, and tertiary benzylamines were calculated to be 31.27, 24.27, and 19.83%, respectively. Hence, the substance isolated was a mixture of benzylamines. The final fractionation of the carefully dried nitrile part of the catalyzate at 752 mm gave: Fraction I, b. p. 92-105°, 3.1 g; Fraction II, b. p. 105-111°, 5.3 g; d^{20}_4 0.8655; $n^{20}D$ 1.4955; Fraction III, b. p. 111-188°, 1.0 g; Fraction IV, b. p. 188-190°, 24.3 g; d^{20}_4 1.0052; $n^{20}D$ 1.5325; residue, 3.5 g.

Part of Fraction II was oxidized with potassium permanganate, and as a result we isolated a white crystalline substance, m. p. 122°; it sublimed without decomposition and was found to be benzoic acid. Hence, Fraction II consisted of toluene, for which the literature [13] gives: b. p. 110.65 - 110.70° (760 mm); d^{20}_4 0.8661; $n^{20}D$ 1.49675. On hydrolysis of Fraction IV we obtained benzoic acid, m. p. 122°. For benzonitrile the literature gives: b. p. 191.3° [14]; d^{20}_4 1.0051 [15]; n^{17}_{20} 1.53225 [16]. On the basis of our results, it must

be considered that Fraction IV consisted of almost pure benzonitrile. In the course of a control experiment 68.0 g of benzyl alcohol was consumed. We obtained 81.0 g of crude catalyzate and 63.4 g of dry catalyzate. In the latter we found 66.7% of nitrile. By the fractionation of 41.5 g of dry catalyzate we isolated 24.3 g (62.2%) of benzonitrile. In Expt. 16-3 in 30 minutes we collected 1616 ml (STP) of gas containing 96.2% of hydrogen.

TABLE 2

Catalytic Nitrile Formation from Benzyl Alcohol

Expt.	Temp. °C	Duration of expt. (min)	Catalyst	Amt. taken for experiment (g)		Amt. of dry catalyzate (g)	Benzonitrile content of catalyzate (%)
				Alcohol	Ammonia		
1	270	30	3% Ni on Al_2O_3	6,8	2,2	5,6	52,9
2	300	30	Ditto	6,8	2,1	5,5	46,5
3	330	30	»	6,8	2,1	5,5	46,0
4	360	30	»	6,8	2,1	5,5	50,8
5	390	30	»	6,8	2,2	5,6	69,0
6	270	30	7,5% Ni on Al_2O_3	6,8	2,2	5,6	22,8
7	300	30	Ditto	6,8	2,1	5,5	55,4
8	330	30	»	6,8	2,1	4,6	48,6
9	360	30	»	6,8	2,1	4,9	42,0
10	390	30	»	6,8	2,1	5,2	51,9
11	270	30	15% Ni on Al_2O_3	6,8	2,1	4,3	31,8
12	300	30	Ditto	6,8	2,2	4,8	53,5
13	330	30	»	6,8	2,1	4,8	53,9
14	360	30	»	6,8	2,2	4,4	49,2
15	390	30	»	6,8	2,1	4,2	44,7
16—1	390	60	3% Ni on Al_2O_3	13,6	4,2	12,0	64,1
16—3	390	60	Ditto	13,6	4,4	12,9	65,8
16—5	390	60	»	13,6	4,4	13,0	69,7

TABLE 3

Catalytic Nitrile Formation from Phenethyl Alcohol

Expt.	Temp. °C	Duration of expt. (min)	Catalyst	Amt. taken for experiment (g)		Amt. of dry catalyzate	Nitrile content of catalyzate (%)
				Alcohol	Ammonia		
1	270	30	3% Ni on Al_2O_3	6,6	2,0	7,0	19,3
2	300	30	Ditto	6,6	2,0	7,4	30,1
3	330	30	»	6,6	2,0	7,3	40,2
4	360	30	»	6,6	2,0	7,4	22,1
5	390	30	»	6,6	2,2	6,0	18,4
6	270	30	7,5% Ni on Al_2O_3	6,6	2,2	6,3	40,0
7	300	30	Ditto	6,6	2,0	6,3	46,7
8	330	30	»	6,6	2,1	6,9	27,6
9	360	30	»	6,6	2,1	5,9	16,2
10	390	30	»	6,6	2,0	5,5	11,9
11	270	30	15% Ni on Al_2O_3	6,6	2,2	6,4	12,3
12	300	30	Ditto	6,6	2,0	6,2	26,3
13	330	30	»	6,6	2,1	6,6	12,6
14	360	30	»	6,6	2,1	5,4	4,2
15	390	30	»	6,6	2,0	4,3	2,9
16-1	300	60	7,5% Ni on Al_2O_3	13,2	4,2	12,3	46,4
16-3	300	60	Ditto	13,2	4,0	12,5	45,3
16-5	300	60	»	13,2	4,0	13,4	46,5

Data from experiments on nitrile formation from phenethyl alcohol are given in Table 3. The optimum temperature for the formation of phenylacetonitrile in presence of a catalyst containing 7.5% of nickel on alumina must be taken as 300°; under these conditions the nitrile content of the catalyzate attains 46%. From 42.0 g of this catalyzate we isolated 1.6 g of amines. In the chloroplatinate prepared from these we found 21.63% of platinum. The platinum contents of the chloroplatinates prepared from primary, secondary, and tertiary phenethylamines were calculated to be 29.93, 22.69, and 18.28%, respectively. Fractionation of the nitrile part of the catalyzate at 749 mm gave: Fraction I, b. p. 108-133°, 3.2 g; Fraction II, b. p. 133-135°, 10.1 g; d^{20}_4 0.8673; $n^{20}D$ 1.4960; Fraction III, b. p. 135-232°, 0.6 g; Fraction IV, b. p. 232-234°, 19.0 g; d^{20}_4 1.01576; $n^{20}D$ 1.5243; residue, 4.5 g.

Fraction II was ethylbenzene, for which the literature [13] gives: b. p. 136.1° (760 mm); d^{20}_4 0.8672; $n^{20}D$ 1.49593. In the hydrolysis of part of Fraction IV we obtained an acid of m. p. 78°. The literature [16] gives for phenylacetonitrile: b. p. 233.5° [17]; d^{20}_4 1.0157 [15]; $n^{17}D$ 1.52432 [16], and also m. p. 78° [18]. Hence, Fraction IV consisted of phenylacetonitrile. In the course of a control experiment 66.0 g of phenethyl alcohol was consumed. This gave 72.3 g of crude catalyzate (62.9 g of dry catalyzate); its nitrile content was 46.1%. For investigation we took 42.0 g of dry catalyzate, from which we isolated 19.0 g (44.8%) of nitrile.

In Expt. 16-3 in 30 minutes we collected 1090 ml (STP) of gas containing 89.8% of hydrogen.

The results of catalytic nitrile formation from 3-phenyl-1-propanol are given in Table 4. The data given show that the optimum conditions for the synthesis of hydrocinnamonitrile are a temperature of 330° and the presence of a catalyst containing 7.5% of nickel on active alumina. Under these conditions the nitrile content of the catalyzate attained 60%. For investigation we took 40.0 g of dry catalyzate; from this we isolated 0.7 g of amines. The chloroplatinate prepared from these contained 23.26% of platinum. The platinum contents of the chloroplatinates of the primary, secondary, and tertiary 3-phenylpropylamines are 28.70, 21.30, and 16.93%, respectively. On fractionation of the nitrile part of the catalyzate we isolated the following fractions: Fraction I, b. p. 130-156°, 2.1 g; Fraction II, b. p. 156-158°, 7.0 g; d^{20}_4 0.8615; $n^{20}D$ 1.4925; Fraction III, b. p. 158-246°, 2.4 g; Fraction IV, b. p. 246-248°, 22.6 g; d^{20}_4 1.0014, $n^{20}D$ 1.5225; this contained 99.9% of hydrocinnamonitrile; residue, 3.6 g.

TABLE 4

Catalytic Nitrile Formation from 3-Phenyl-1-propanol

Expt.	Temp. °C	Duration of expt. (min)	Catalyst	Amt. taken for experiment (g)		Amt. of dry catalyzate	Nitrile content of catalyzate (%)
				Alcohol	Ammonia		
1	300	30	3% Ni on Al_2O_3	6,6	1,6	6,3	12,5
2	330	30	Ditto	6,6	1,8	6,7	44,8
3	360	30	»	6,6	1,8	5,7	46,1
4	390	30	»	6,6	1,6	5,0	33,5
5	300	30	7,5% Ni on Al_2O_3	6,6	1,8	5,3	58,8
6	330	30	Ditto	6,6	1,6	5,2	62,4
7	360	30	»	6,6	1,8	6,1	45,8
8	390	30	»	6,6	1,8	5,2	33,8
9	270	30	15% Ni on Al_2O_3	6,6	1,8	4,8	37,4
10	300	30	Ditto	6,6	1,6	5,3	54,1
11	330	30	»	6,6	1,6	5,6	48,0
12	360	30	»	6,6	1,8	5,4	34,6
13	390	30	»	6,6	1,8	5,4	32,7
14-1	330	60	7,5% Ni on Al_2O_3	13,2	3,4	10,4	59,2
14-3	330	60	Ditto	13,2	3,4	11,6	60,1
14-5	330	60	»	13,2	3,4	14,4	61,3

Fraction II was propylbenzene. For propylbenzene the literature gives: b. p. 158° (760 mm) [19]; d^{20}_4 0.8617 [20]; $n^{20}D$ 1.4925 [16]. On hydrolysis of a part of Fraction IV we obtained an acid of m. p. 48°.

According to the literature hydrocinnamonitrile has b. p. 246-248° [21] and d^{18} 1.0014 [22], and hydrocinnamic acid has m. p. 48° [23]. Hence, Fraction IV has hydrocinnamonitrile.

In the course of a control experiment 66.0 g of 3-phenyl-1-propanol was consumed. This gave 72.3 g of crude catalyzate (57.1 g of dried catalyzate), in which we found 60.5% of nitrile. From 40.0 g of dry catalyzate we isolated 22.6 g (50.8%) of hydrocinnamonitrile. In Expt. 14-3 in 30 minutes we collected 768 ml (STP) of gas containing 70.8% of hydrogen.

The experiments on the formation of nitriles from aromatic and aliphatic [7] alcohols under the action of ammonia show that under our conditions the small amount of amines formed is independent of the amount of nitrile obtained. We therefore suppose that the primary amine is first formed directly from the alcohol:

$$ArCH_2OH + NH_3 \longrightarrow ArCH_2NH_2 + H_2O.$$

There may then be further formation of secondary and tertiary amines by the scheme: $2ArCH_2NH_2 \rightarrow$ $\rightarrow (ArCH_2)_2NH + NH_3$

$$(ArCH_2)_2NH + ArCH_2NH_2 \longrightarrow (ArCH_2)_3N + NH_3.$$

At the same time part of the ammonia decomposes on the catalyst surface into nitrogen and hydrogen $2NH_3 \rightarrow N_2 + 3H_2$, and the latter, together with hydrogen formed in the main nitrile-formation reaction, reduces some of the nitrile formed into the aromatic hydrocarbon:

$$ArCN + 3H_2 \longrightarrow ArCH_3 + NH_3.$$

The formation of toluene and ammonia on passage of benzonitrile vapor and hydrogen over nickel at 200° was observed by Sabatier and Senderens [24].

SUMMARY

1. The optimum conditions were found for the synthesis of benzonitrile, phenylacetonitrile, and hydrocinnamonitrile by reaction of ammonia with benzyl, phenethyl, and 3-phenylpropyl alcohols over a nickel-alumina catalyst in a flow system.

2. In presence of a 3% nickel-alumina catalyst at 390° the yield of benzonitrile attains 51.7%. The maximum yields of phenylacetonitrile (at 300°) and hydrocinnamonitrile (at 330°) are obtained by carrying out the nitrile formation over a 7.5% nickel-alumina catalyst and are 44.8 and 50.8%, respectively.

3. A hypothesis was advanced on the mechanism of the formation of a small amount of amines and aromatic hydrocarbons as by-products in the nitrile synthesis.

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CATALYTIC DEHYDROGENATION OF BRANCHED C_6 PARAFFINS

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The present work forms a continuation of our previous investigation on the dehydrogenation of hydrocarbons of various structures in presence of an alumina-chromia-potassia catalyst [1]. It was shown that the yield of olefins obtained from branched C_6 paraffins is considerably higher than that obtained from hexane. However, the nature of the unsaturated hydrocarbons formed was not determined; neither was the individual composition of the gases. The present investigation remedies these deficiencies. Also, a thermodynamic calculation is carried out on the reaction C_6 paraffins $\rightleftharpoons$ C_6 olefins, and the theoretical and experimental yields of branched C_6 olefins are compared.

EXPERIMENTAL

The 2- and 3-methylpentanes and the 2,3-dimethylbutane taken for investigation were synthesized with the aid of the Grignard reaction. 2,2-Dimethylbutane was prepared by the pyrolysis of pinacolyl acetate [2]. After being distilled carefully through a column of 40-plate efficiency, the hydrocarbons had constants coinciding with those given in the literature [3]. The branched C_6 paraffins were brought into contact with an alumina-chromia-potassia catalyst, whose composition and method of preparation are described in our preceding communication (Catalyst 6) [4]. The experiments were carried out in a flow system at atmospheric pressure at 500° with a space velocity of 0.5 hr^{-1}; the volume of catalyst in the tube was 30 ml, the amount of hydrocarbon taken in each experiment was 100 ml, and the experiment lasted about seven hours. After each experiment the catalyst was regenerated by oxidation with air for 4-5 hours at 700°. The liquid catalyzate was analyzed for the contents of alkenes, alkadienes, and aromatic hydrocarbons by methods which we have described previously [5].

Table 1 gives the properties of the catalyzates from C_6 branched paraffins, and Table 2 gives the compositions of the gases formed. For comparison we give the data for n-hexane. As will be seen from Table 1, in the dehydrogenation of 2- and 3-methylpentanes and 2,3-dimethylbutane 34-40% of unsaturated hydrocarbons is obtained, whereas from hexane only 14%; at the same time about 2% of aromatic hydrocarbons was obtained from the branched C_6 paraffins, but 43% from hexane. From 2,2-dimethylbutane was obtained 15% of unsaturated hydrocarbons. No aromatic hydrocarbons were detected in the 2,2-dimethylbutane catalyzate.

The gases formed from 2- and 3-methylpentanes and 2,3-dimethylbutane contained 84-90% of hydrogen, 9-12%, in all, of methane, ethane, and propane, and 1-4% of other olefins and paraffins.

The gas from 2,2-dimethylbutane contained 72.6% of hydrogen, 21.2% of C_1-C_3 alkanes, and 6.2% of other hydrocarbons. On the basis of these results it may be stated that, under the given conditions, 2,2-dimethylbutane is less stable than other C_6 paraffins. Investigation of the composition of the liquid catalyzate from 2,2-dimethylbutane confirmed this conclusion.

The catalyzates from the C_6 paraffins were fractionated through a column of 40-plate efficiency, and fractionation curves were determined at the same time. For the fractionation 100 ml of catalyzate was taken. In

TABLE 1.

Properties of Catalyzates from C_6 Paraffins

Hydrocarbon	Yield of catalyzate	n_D^{20}	Olefin content (%)	Diene content	Aromatic content	Amt. of gas (liters at STP)
2-Methylpentane	86.0	1.3830	32.0	2.3	2.2	10,900
3-Methylpentane	88.3	1.3887	38.9	0.7	1.8	12,160
2,3-Dimethylbutane	89.2	1.3875	40.1	4.5	1.5	11,230
2,2-Dimethylbutane	92.9	1.3710	14.6	0.5	Nil	4.340
Hexane	86.6	1.4220	13.7	1.0	42.6	34.400

TABLE 2.

Compositions of Gases Obtained in the Catalytic Treatment of C_6 Paraffins

Hydrocarbon	H_2	CH_4	C_2H_6	C_2H_4	C_3H_6	C_4H_8 and C_4H_{10}	C_4H_8 and i-C_5H_{12}
2-Methylpentane	83,9	5,1	3,1	0,6	4,2	2,2	0,9
3-Methylpentane	89,6	5,0	3,8	0,2	0,3	0,5	0,6
2,3-Dimethylbutane	86,5	5,6	1,1	0,2	4,6	1,8	0,2
2,2-Dimethylbutane	72,6	8,8	11,2	1,7	1,2	2,6	1,9
Hexane	96,9	0,9	0,8	—	0,8	0,4	0,2

TABLE 3.

Results of the Analysis of the Hydrocarbon Mixture with the Aid of Gas-Liquid Chromatography

Compositions of Mixture	Taken (% by wt.)	Found % by wt.)
Isopentane	6.5	6.0
Pentane	6.8	5.6
3,3-Dimethyl-1-butene	9.9	11.0
2,3-Dimethylbutane	9.1	10.8
Hexane	60.0	59.9
2.3-Dimethyl-2-butene	7.7	6.7

the fractions we determined n_D^{20}, d_4^{20} and iodine value. They were then analyzed with the aid of Raman spectra. In addition, fractions of the 2-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane catalyzates were analyzed by the method of gas-liquid chromatography. For this purpose we used a column, length 2 m and diameter 6 mm, filled with kieselguhr moistened with tritolylphosphate, a modified micro-flame detector [6], and hydrogen as carrier gas. The working temperature of the column was 20° or 56°.

We first determined the chromatograms of all the hexane isomers, pentane, isopentane, and the paraffins and alkadienes at our disposal, namely: 3,3-dimethyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, 2-methyl-1-pentene, 2,3-dimethyl-1,3-butadiene, and also other paraffins, olefins, and dienes not found in the catalyzates investigated. From these hydrocarbons we prepared mixtures varying in the nature and amounts of the components, and these were then analyzed with the aid of chromatograms. As an example we give the chromatogram of one of these artificial mixtures (Fig. 1), and also data on the composition of this mixture and the results of the analysis (Table 3). As will be seen from Table 3 the accuracy of the analysis is quite satisfactory.

The quantitative determination of the remaining olefins and dienes (4-methyl-2-pentene, 2-methyl-2-pentene, 4-methyl-1-pentene, and 4-methyl-2,4-pentadiene) by the method of gas-liquid chromatography was carried out on the basis of qualitative data obtained with the aid of Raman spectra. Fig. 1 gives the chromatograms for some of the fractions. Tables 4-7 give the properties and compositions of the fractions, determined by various methods.

Hence, apart from unchanged hydrocarbons, the paraffins, olefins, dienes, and aromatic hydrocarbons indicated below were detected in the catalyzates from branched C_6 paraffins.

TABLE 4.

Compositions and Properties of Fractions of the 2-Methylpentane Catalyzate

Fraction	Boiling range (°C at 760 mm)	Yield (% by vol.)	n_D^{20}	d_4^{20}	Iodine volume	Unsaturated content (% by wt.)	Results of analysis with the aid of	
							Raman spectra	Gas-liquid chromatography (%)
I	42.6–60.1	12.5	1.3740	0.6540	112.8	37.3	2-methylpentane 4-methyl-1-pentene 4-methyl-2-pentene	2-methylpentane 66 4-methyl-1-pentene 27 4-methyl-2-pentene 7 isopentane Traces
II	60.1–61.5	70.5	1.3760	0.6578	50.1	16.8	2-methylpentane 2-methyl-1-pentene	2-methylpentane 81 2-methyl-1-pentene 3 4-methyl-1-pentene 10 4-methyl-2-pentene 6
III	61.5–65.1	7.5	1.3850	0.6697	154.2	51.2	2-methylpentane 2-methyl-2-pentene	2-methylpentane 47 2-methyl-2-pentene 47 4-methyl-2-pentene 6 (traces of 4-methyl-1-pentene)
IV	65.1–75.1	8.0	1.4245	0.7130	283.3	93.7	2-methyl-2-pentene 2-methyl-2,4-pentadiene benzene	2-methylpentene 4 2-methyl-2-pentene 30 2,3-dimethyl-2-butene 10 2-methyl-2,4-pentadiene 41 benzene 14
Residue		1.0	1.4775	–	182.9	60.5	Not analyzed	

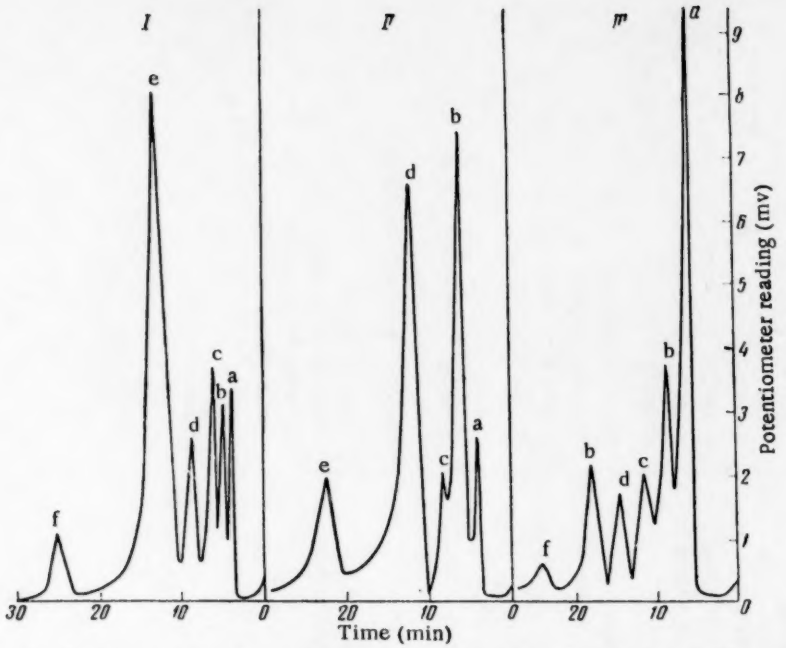
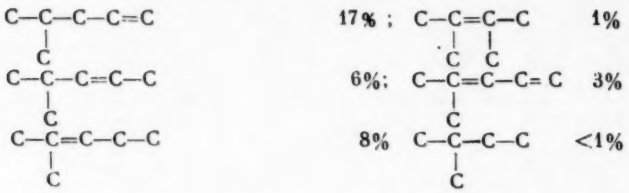


Fig. 1. Chromatograms of an artificial hydrocarbon mixture and of some fractions of catalyzates from branched C_6 paraffins: I, Artificial mixture: a) isopentane; b) pentane; c) 3,3-dimethyl-1-butene; d) 2,3-dimethylbutane; e) hexane; f) 2,3-dimethyl-2-butene. II, Fraction IV of catalyzate from 2-methylpentane (temp. of column 56°): a) 2-methylpentane; b) 2-methyl-2-pentene; c) pentene; c) 2,3-dimethyl-2-butene; d) 2-methyl-2,4-pentadiene; e) benzene. III, Fraction III of catalyzate from 2,2-dimethylbutane: a) 2,2-dimethylbutane + 3,3-methyl-2-pentene (cis and trans); e) 2-methyl-2-pentene; f) 2,3-dimethyl-1,3-butadiene.

2-Methylpentane Catalyzate



Benzene 1%

3-Methylpentane Catalyzate

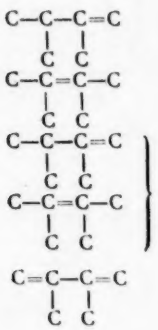
Benzene 1%

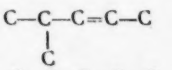
TABLE 5.

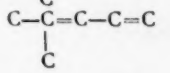
Compositions and Properties of Fractions of the 3-Methylpentane Catalyzate

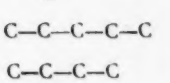
Fraction	Boiling range (°C at 760 mm)	Yield (% by vol.)	n_D^{20}	d_4^{20}	Iodine value	Unsaturated content (% by wt.)	Results of analysis with aid of Raman spectra
I	35.5–62.5	10.0	1.3776	0.6638	85.0	28.1	3-Methyl-pentane 3-methyl-1-pentene
II	62.5–63.0	59.4	1.3790	0.6665	43.2	14.3	3-methylpentane 3-methyl-1-pentene and 3-methyl-2-pentene
III	63.0–67.5	7.5	1.3793	0.6681	47.1	15.5	3-methylpentane and 3-methyl-2-pentene
IV	67–5	5.4	1.4015	0.6941	296.0	97.0	Not investigated
V	67.5–74.5	16.9	1.4032	0.7049	263.0	87.0	The main product was 3-methyl-2-pentene. A small amount of 2-ethyl-1-butene could be present. Benzene and 3-methylpentane were also detected
Residue		0.8	1.5405	–	119.6	39.6	Not investigated

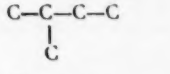
2, 3 -Dimethylbutane Catalyzate



16–17%;  3%

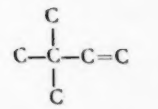
10%;  2%

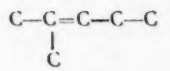
4%;  <1%

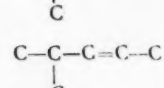
 <1%

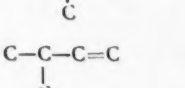
3%; Benzene <1%

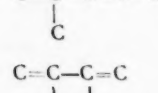
2,2-Dimethylbutane Catalyzate

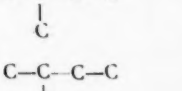


8%;  2%



3–4%;  <1%



<1%;  <1%

The results obtained by analysis of the compositions of the catalyzates give us reason to suppose that under the given conditions dehydrogenation of all of the C_6 paraffins results in the formation of olefins that in the main contain six carbon atoms. In the dehydrogenation of 3-methylpentane, no skeletal isomerization was observed; in the dehydrogenation of 2-methylpentane and 2,3-dimethylbutane, isomerization occurred only to a small extent;

TABLE 6.

Compositions and Properties of Fractions of the 2,3-Dimethylbutane Catalyzate

Fraction	Boiling range (°C at 760 mm)	Yield (% by vol.)	n_D^{20}	d_4^{20}	Iodine volume	Unsaturated content (% by wt.)	Results of analysis with the aid of	
							Raman spectra	Gas-liquid chromatography (%)
I	47.0–56.9	16.3	1.3820	0.6662	182.0	60.2	2,3-Dimethylbutane 2,3-Dimethyl-1-butene Traces of 4-methyl-2-pentene	Pentane and isopentane (about 1% of each); 2,3-dimethylbutane 37%; 2,3-dimethyl-1-butene 61%
II	56.9–58.5	57.5	1.3765	0.6632	47.8	15.9	2,3-Dimethylbutane and 2,3-dimethyl-1-butene	2,3-Dimethylbutane 81% 2,3-dimethyl-1-butene 13% 4-methyl-1-pentene 6%
III	58.5–66.9	6.2	1.3905	0.6773	191.4	63.3	2,3-Dimethyl-1-butene, 2,3-dimethyl-2-butene, and 2,3-dimethylbutane	Not analyzed
IV	66.9–75.1	16.9	1.4185	0.7140	309.0	100.0	2,3-Dimethyl-2-butene 60% 2,3-Dimethyl-1,3-butadiene 20% 4-methyl-1,3-pentadiene 10% 2,3-dimethylbutane and traces of benzene	2,3-Dimethyl-2-butene and dimethyl-1,3-butadiene 82% 4-methyl-1,3-pentadiene 10% benzene and possibly 2-methyl-1-pentene 4%
Residue		1.9	1.4915	—	158.6	52.5	Not analyzed	

TABLE 7.

Compositions and Properties of Fractions of the 2,2-Dimethylbutane Catalyzate

Fraction	Boiling range (°C at 760 mm)	Yield (% by vol.)	n_D^{20}	d_4^{20}	Iodine volume	Unsaturated content (% by wt.)	Results of analysis with the aid of	
							Raman spectra	Gas liquid chromatography (%)
I	38.6–48.9	23.1	1.3690	0.6499	62.1	20.5	2,2-Dimethylbutane and 3,3-dimethyl-1-butene	2,2-Dimethylbutane 78%, 3,3-dimethyl-1-butene 19%, 3-methyl-1-butene 2%, isopentane 1%
II	48.9–50.5	58.5	1.3685	0.6494	13.5	4.4	2,2-Dimethylbutane and 3,3-dimethyl-1-butene	2,2-Dimethylbutane 95%, 3,3-dimethyl-1-butene 5%
III	50.5–61.8	14.6	1.3875	0.6640	82.9	27.4	2,2-Dimethylbutane and 4-methyl-2-pentene (cis and trans) 21%	2,2-Dimethylbutane 49%, 4-methyl-2-pentene (cis and trans) 21%, 2-methylpentane 17%, 2-methyl-2-pentene 12%, 3,3-dimethyl-1-butene 1%, 2,3-dimethyl-1,3-butadiene 1%
Residue		1.5	1.3856	–	123.4	40.8	Not analyzed	

TABLE 8.

Thermodynamic Calculation of the Reaction Hexane Isomers ⇌ Hexene Isomers

Paraffin	Olefin	600 °K = 327 °C		700 °K = 427 °C		800 °K = 527 °C		900 °K = 627 °C		1000 °K = 727 °C	
		$\log K_p$	x	$\log K_p$	x	$\log K_p$	x	$\log K_p$	x	$\log K_p$	x
2-Methylpentane	2-Methyl-1-pentene	−3,15780	2,6	−1,61401	15,4	−0,50809	48,7	0,37636	83,9	1,07300	96,0
	2-Methyl-2-pentene	−2,93924	3,4	−1,52036	17,1	−0,45346	51,0	0,35208	83,2	1,00744	95,4
	4-Methyl-2-pentene (cis)	−3,74053	1,3	−2,20717	7,8	−1,08174	27,7	−0,18211	63,0	0,50481	87,3
	4-Methyl-2-pentene (trans)	−3,55842	1,7	−2,08229	9,1	−0,94515	31,9	−0,08498	67,2	0,59223	89,2
	4-Methyl-1-pentene	−4,50539	0,6	−2,89399	3,6	−1,68269	14,3	−0,54633	47,0	0,04589	72,6
	Over-all yield of C_6 olefins	−2,63451	4,8	−1,15364	25,5	−0,05578	68,4	0,80566	93,0	1,48033	98,4
3-Methylpentane	2-Methyl-1-pentene	−3,78788	1,3	−2,07203	9,1	−0,74574	39,0	0,30594	81,8	1,16259	96,7
	4-Methyl-2-pentene (cis)	−2,87733	3,6	−1,44855	18,5	−0,39062	53,8	0,45163	86,0	1,11889	96,4
	4-Methyl-2-pentene (trans)	−2,69522	4,5	−1,26124	22,8	−0,19941	62,2	0,62160	89,8	1,29371	97,6
	2-Ethyl-1-butene	−3,38724	2,0	−1,88561	11,3	−0,71842	40,1	0,16026	76,9	0,87850	94,0
	Over-all yield of C_6 olefins	−2,40670	6,2	−0,95133	31,7	0,14904	76,5	1,01044	95,5	1,73969	99,1
2,3-Dimethylbutane	2,3-Dimethyl-1-butene	−2,99390	3,2	−1,47353	18,0	−0,28955	58,2	0,59034	89,2	1,33086	97,7
	2,3-Dimethyl-2-butene	−2,92104	3,4	−1,50475	17,4	−0,45345	51,0	0,35694	83,3	1,02491	95,6
	Over-all yield of C_6 olefins	−2,65600	4,6	−1,18782	24,7	−0,06278	68,1	0,79027	92,8	0,50532	98,5
2,2-Dimethylbutane	2,3-Dimethy-1-butene	−4,60373	0,5	−2,98764	3,2	−1,73459	13,5	−0,76000	38,5	0,00874	71,1

TABLE 9.

Experimental and Equilibrium Yields of C_6 Olefins at 500°

Hydrocarbon	Yield (mole fraction on hydrocarbon passed)							K_p	Equilibrium concn. of C_6 olefins (x)	
	C_6H_{14} n_1	C_6H_{12} n_2	H_2 n_3	Gas n_4	C_4H_8 n_5	C_4H_{10} n_6	Σn_i		by Equation (1)	by Equation (2)
1	2	3	4	5	6	7	8	9	10	11
2-Methylpentane	0,415	0,386	0,723	0,130	0,057	0,021	1,732	0,4787	0,575	0,422
3-Methylpentane	0,381	0,478	0,699	0,103	0,049	0,007	1,717	0,7430	0,653	0,530
2,3-Dimethylbutane	0,412	0,417	0,723	0,083	0,031	0,040	1,726	0,4677	0,552	0,434

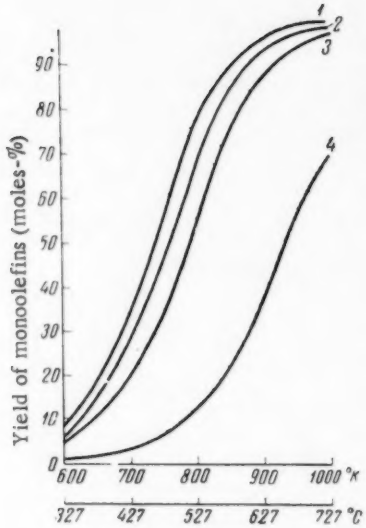


Fig. 2. Theoretical yields of hexene isomers from hexane isomers (according to Equation (1): 1) from 3-methylpentane; 2) from 2-methyl-pentane and 2,3-dimethylbutane; 3) from hexane; 4) from 2,2-dimethylbutane.

but in the catalytic treatment of 2,2-dimethylbutane, olefins were obtained of which about one-half consisted of isomerization products, namely, 4-methyl-2-pentene, 2-methyl-2-pentene, and 2,3-dimethyl-1,3-butadiene.

THERMODYNAMIC CALCULATION

From the free energies of formation for all the isomeric C_6 olefins [7] the equilibrium constants K_p for the dehydrogenation of C_6 paraffins were calculated, and from the equation

$$K_p = \frac{x^2}{1 - x^2} \qquad (1)$$

the corresponding yields ($\underline{x}$) of C_6 olefins were calculated. The results are presented in Table 8. Fig. 2 shows the relation of the equilibrium yields of C_6 olefins, and also of hexenes obtained from hexane, to the temperature. A further calculation was made of the theoretical yield for all C_6 olefins (account being taken of side reactions [8]) from the equation

$$K_p = \frac{x\,(n_3 - n_2 + x)}{(n_1 + n_2 - x)\,(\Sigma n_i - n_2 + x)}, \qquad (2)$$

in which $\underline{n}$ denotes mole fractions of reaction products: n_1-unchanged C_6 paraffin; n_2-C_6 olefins; n_3-dienes with conjugated bonds; $\Sigma n_i = n_1 + n_2 + n_3 + n_4 + n_5 + n_6$. The values of K_p in this equation were determined by graphical extrapolation from the data of Table 8.

In Table 9 we give the experimental* (Column 3) and equilibrium yields of C_6 olefins according to Equation (1) (Column 10) and according to Equation (2) (Column 11). In view of the fact that, in the course of catalytic treatment, 2,2-dimethylbutane undergoes change in its carbon skeleton to a considerable extent, no calculations were made for it with the aid of Equation (2). It will be seen from the results that the experimental yields of C_6 olefins are close to the equilibrium values. We have previously [8, 9] investigated the dehydrogenation of pentane and isopentane, which was carried out in presence of the same catalyst. It was shown that under the experimental conditions (500° at a space velocity of 0.5 hr^{-1}) this reaction also almost attains a state of equilibrium.

The gas analysis was carried out by R. N. Shafran, to whom we express our sincere thanks.

*For the calculations we took analytical results on portions of catalyzate of maximum olefin content and corresponding to 10 ml of the C_6 paraffin passed.

SUMMARY

1. An investigation was made of the dehydrogenation of C_6 paraffins at 500° with a space velocity of 0.5 hr^{-1} over an alumina-chromia-potassia catalyst which had previously been shown to have high activity for the dehydrogenation of pentane and isopentane.

2. 2-Methylpentane, 3-methylpentane, and 2,3-dimethylbutane are dehydrogenated with formation of the corresponding C_6 olefins in yields of 32-40% on the catalyzate. Under certain conditions the experimental yields of C_6 olefins are close to the equilibrium values.

3. In the dehydrogenation of 2,2-dimethylbutane 15% of unsaturated hydrocarbons is formed in the catalyzate, and of this about one-half consists of products of the isomerization of the carbon skeleton.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

EFFECT OF THE SPECIFIC SURFACE OF PLATINIZED ALUMINUM SILICATE ON THE CONVERSION OF NONANE

COMMUNICATION 2. CHANGE OF THE CATALYTIC ACTIVITY OF PLATINIZED ALUMINUM SILICATE ON TREATMENT OF THE CARRIER WITH STEAM

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In two of our previous investigation [1, 2] we studied the tranformations of nonane over platinized aluminum silicate as a function of temperature and the specific surface of the catalyst. It was shown that at a hydrogen pressure of 20 atm and temperatures of 360-440° over catalysts containing 1% platinum whose carriers were prepared by the roasting of aluminum silicate at high temperatures (860-990°) in a stream of hydrogen and which had specific surfaces of 30, 80, 170, and 260 sq. m/g isomerization and hydrocracking occurred, and at 400° and higher aromatization began to play a part.

Over catalysts having specific surface of 170 and 260 sq. m/g the yield of branched C_9 paraffins fell with rise in temperature from 360° to 400°; over a catalyst having a specific surface of 80 sq. m/g the yield of branched C_9 paraffins was at a maximum at 400°, and over a catalyst having a specific surface of 30 sq. m/g the yield of the same products rose in the range 360-440°. It was shown that with reduction in the specific surface of the catalyst at constant temperature the yield (on the original nonane) of conversion products fell, whereas the content of branched paraffins in the catalyzate increased, so that the contribution of hydrocracking in the over-all conversion fell. Hence, in these investigations it was shown that as the specific surface of the catalyst increased the temperature at which hydrocracking became a predominant reaction became higher and higher. Also, over catalysts of low specific surface it was possible to obtain aromatic hydrocarbons in yields of up to 10% even before the lowering of the yield of branched alkanes at temperatures above 400°. Under our conditions we succeeded in obtaining branched C_9 alkanes in yields of up to 34-35% on the original hydrocarbon.

Continuing our investigation on the effect of the specific surface of the catalyst on the extent of the conversion of hydrocarbons, in the present work we decided to study the transformations of nonane over aluminum silicate catalysts differing in specific surface. One of these catalysts was prepared by treating commercial aluminum silicate with steam at 820° with the object of raising the yield of branched C_9 paraffins and reducing the amount of hydrocracking. At a hydrogen pressure of 20 atm, which we used in our previous work, hydrocracking was considerable, even at low temperature, and in the present work we therefore used a hydrogen pressure of 10 atm.

Our experiments confirmed the regularities established in our previous investigation [2]. Thus, over 0.5% Pt–aluminum silicate having a specific surface of 320 sq. m/g * we succeeded in obtaining 53% of branched C_9 paraffins at a temperature of 380°, whereas over a catalyst having a specific surface of 60 sq. m/g (K-2) the same yield of branched paraffins was reached only at 450°.

*For the sake of brevity this catalyst will in future be referred to as K-1, and the catalyst having a specific surface of 60 sq. m/g as K-2.

TABLE 1

Yield of Main Transformation Products of Nonane (% on original hydrocarbon)

Specific surface of catalyst (sq. m/g)	320			60				
Temperature (°C)	360	380	400	360	380	400	420	450
Yield of catalyzate	92,1	89,3	84,1	98,7	95,4	90,6	89,9	85,1
Conversion	51,5	82,2	100	31,6	49,5	58,8	73,9	87,9
Yield of branched C_9 paraffins	33,5	53,1	44,0	28,7	39,3	46,2	52,4	54,1
Unchanged nonane	48,5	17,8	0,0	68,4	50,5	40,2	26,1	10,1
Yield of light hydrocarbons up to C_5	5,3	9,5	12,1	—	0,30	4,3	8,2	9,1
Yield of C_5 hydrocarbons	2,6	7,2	13,7	—	1,1	1,9	3,9	8,3
Intermediate fraction of b.p. 40-128°	3,8	7,7	12,1	—	0,9	4,2	5,5	7,2
Total yield of hydrocracking products	11,7	24,9	45,7	—	5,0	10,6	16,6	25,3
Yield of aromatic hydrocarbons	—	Traces	2,9	—	Traces	2,2	5,3	7,9

TABLE 2

Properties and Composition of C_9 Paraffins Isolated from the Catalyzate Obtained over Catalyst K-2 at 450°

Fraction	B.p. (°C at 750 mm)	Yield (% on original nonane)	n_D^{20}	d_4^{20}	Composition according to Raman analysis
I	128—135	2,8	1,4028	0,7157	50% trimethylhexanes 50% dimethylheptanes
II	135—140	3,2	1,4050	0,7202	75% dimethylheptanes 25% trimethylhexanes
III	140—145	20,1	1,4057	0,7194	45% dimethylheptanes 55% methyloctanes
IV	145—150	28,0	1,4052	0,7182	80% methyloctanes 20% nonane
V	150—150,5	7,0	1,4055	0,7179	75% nonane 25% methyloctanes

Hence, reduction in the specific surface of the catalyst enables us to carry out the process at higher temperatures without fear of causing hydrocracking.

EXPERIMENTAL

As carrier for the preparation of platinum catalysts we used a standard commercial aluminum silicate cracking catalyst of composition: Al_2O_3 – 11.91%; SiO_2 – 85.35%; Na_2O – 0.21%; Fe_2O_3 – 0.15%; CaO – 0.44%; MgO – 0.63%; SO_3 – 1.07%; bulk density 0.7 g/cc; specific surface 320 sq. m/g. Ferric oxide impurity was removed from the aluminum silicate by boiling it in a water bath with dilute (1:2) hydrochloric acid. After the carrier had been washed and roasted at 500° its specific surface remained unchanged. A catalyst carrier having a specific surface of 60 sq. m/g was prepared by treating the washed and roasted aluminum silicate with steam at 820° for four hours. The specific surfaces of carriers were determined by a dynamic method from the absorption of benzene vapor at 20° [3].

Catalysts were prepared by impregnation of the carriers with a dilute solution of H_2PtCl_6. The products were dried at 110° for five hours and then reduced in a stream of electrolytic hydrogen at 330° for ten hours. The platinum content of the catalysts was 0.5%.

The nonane taken for catalytic treatment had the following properties: b. p. 149–150.4° (745 mm); n_D^{20} .

1.4058; d_4^{20} 0.7178; found MR 43.76; C_9H_{20} calculated MR 43.87; which are in good accord with date in the literature [4]. Determination of infrared absorption spectra showed that the nonane contained no other C_9 paraffins.

The apparatus used is described in one of our earlier papers[1]. The experiments were carried out at temperatures of 360°, 380°, 400°, 420°, and 450°; hydrogen pressure 10 atm; space velocity 1 hr^{-1}; molar ratio of hydrocarbon to hydrogen 1:5. The amount of nonane taken in an experiment was 105-145 g. Each experiment was carried out over a fresh portion of catalyst.

Investigation of Catalyzates. At the end of each experiment the catalyzate obtained was debutanized to removed C_1-C_4 hydrocarbons, which collected in a gas holder and were subjected to chromathermographic analysis. The fraction boiling up to 40° (isopentane and pentane) was distilled from the debutanized catalyzate. Aromatic hydrocarbons were separated by chromatographic absorption on silica gel. The mixture of aromatic hydrocarbons was then fractionated through a column of 35-plate efficiency, and the fractions isolated were investigated by means of Raman spectra. The naphthene-paraffin part was fractionated through the same 35-plate column into narrow fractions, which were characterized by their physical properties (n..and d..). Fractions containing branched C_9 paraffins were analyzed quantitatively by determining their infrared absorption spectra. The results of the investigation of the catalyzates are presented in Tables 1 and 2 and in Figures 1-3.

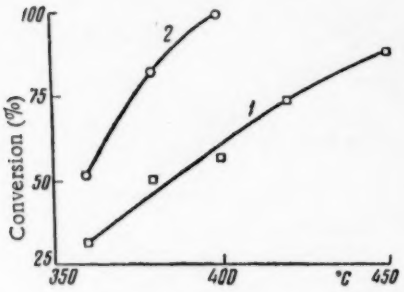

Fig. 1. Relation of conversion of nonane to temperature: 1) 60 sq. m/g; 2) 320 sq. m/g.

From the data in Table 1 and Fig. 1 it can be seen that the rate of the increase of the conversion of nonane with rise in temperature is much greater over the catalyst of specific surface 320 sq. m/g than over the catalyst of specific surface 60 sq. m/g.

Thus, a rise in temperature of 40° from 360° to 400° leads to an increase in conversion of 50% in the case of the first catalyst, whereas over the second catalyst an increase in conversion of 56% corresponds to a change in temperature of as much as 90°.

From Table 1 and Fig. 2 it will be seen that over the catalyst of specific surface 320 sq. m/g the yield of hydrocracking products increases much more rapidly with rise in temperature than over the catalyst of specific surface 60 sq. m/g.

Thus, a rise in temperature of 40° from 360° to 400° leads to an increase in conversion of 50% in the case of the first catalyst, whereas over the second catalyst an increase in conversion of 56% corresponds to a change in temperature of as much as 90°.

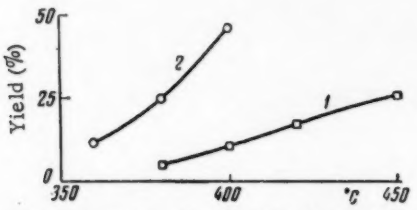

Fig. 2. Relation of yield of hydrocracking products to temperature: 1) 60 sq. m/g; 2) 320 sq. m/g.

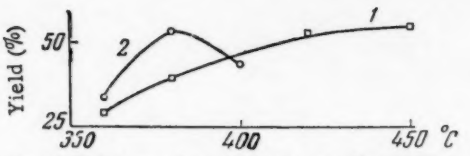

Fig. 3. Relation of yield of C_9 paraffins to temperature: 1) 60 sq. m/g; 2) 320 sq. m/g.

From Table 1 and Fig. 2 it will be seen that over the catalyst of specific surface 320 sq. m/g the yield of hydrocracking products increases much more rapidly with rise in temperature than over the catalyst of specific surface 60 sq. m/g. For this reason at a given temperature the yield of hydrocracking products is much greater over Catalyst K-1 (specific surface 320 sq. m/g) than over Catalyst K-2 (specific surface 60 sq. m/g).

At high temperatures (420-450°) hydrocracking no longer plays a determining part over a catalyst of specific surface 60 sq. m/g, and this makes it possible to obtain branched C_9 paraffins in fairly high yield (54% at 450°) (Fig. 3). Over a catalyst of specific surface 320 sq. m/g the maximum yield of branched C_9 paraffins (53%) is attained at 380°. As aromatization becomes appreciable only at 400° and higher, over a catalyst of specific surface 60 sq. m/g aromatic hydrocarbons may be obtained before the reduction in the yield of branched C_9 paraffins occurs.

The analysis of the gases obtained in the debutanization showed that they consisted mainly of propane and butane with small amounts of propene and butenes. Thus, the gas obtained at 380° over the catalyst of specific surface 320 sq. m/g contained 35% of propane, 60% of butane, and 5% of C_3-C_4 unsaturateds, and the gas obtained at the same temperature over the catalyst of specific surface 60 sq. m/g was of approximately the same composition, but contained a somewhat smaller amount of unsaturateds. The intermediate fraction, b.p. 40-128°, consisted of a mixture of C_6-C_8 unsaturated hydrocarbons.

As stated above, the paraffin part of the catalyzate was fractionated into narrow fractions and then analyzed with the aid of Raman spectra. In Table 2 we give an example of such a fractionation of C_9 paraffins obtained at 450° over a catalyst of specific surface 60 sq. m/g.

After their separation by chromatography on silica gel the aromatic hydrocarbons were united and fractionated through a colum of 35-plate efficiency. We then isolated fractions boiling in the ranges 152-163° and 163--170° at 750 mm. These fractions comprised 84.6% of the total amount of aromatic hydrocarbons. The fraction of b.p. 152-163° (7.6 g) had 0.8628 and 1.4941, and according to Raman spectrum data it consisted of 50% of m-ethyltoluene, 27% of p-ethyltoluene, and 23% of cumene. The fraction of b.p. 163-170° (6.1 g) had d_4^{20} 0.8735 and n_D^{20} 1.5127, and it contained about 80% of 1,2,4-trimethylbenzene and 20% of mesitylene.

SUMMARY

1. An investigation was made of the catalytic transformation of nonane over two samples of 0.5% platinum--aluminum silicate catalyst differing in specific surface at 360-450° under a hydrogen pressure of 10 atm in a flow system.

2. It was found, as in previous work, that the extent of hydrocracking of hydrocarbons diminishes considerably with reduction in the specific surface of the catalyst.

3. The conditions were found for the isomerization of nonane into branched C_9 paraffins in yields of up to 54%. Over a catalyst of specific surface 320 sq. m/g (K-1) this yield was reached at 380°, and over a catalyst of specific surface 60 sq. m/g (K-2) this yield of branched C_9 paraffins was obtained at 450°. Under these conditions the total yields of hydrocracking products were 45.7% over Catalyst K-1 and 25.3 over Catalyst K-2.

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TRANSFORMATIONS OF HEXANE, METHYLCYCLOPENTANE, AND CYCLOHEXANE IN PRESENCE OF A RHENIUM-ALUMINA CATALYST AND OF HYDROGEN UNDER PRESSURE

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Increasing attention has been given recently to the utilization of rare elements, not only in the metallurgical, aviation, and machine-construction industries, but also in the chemical industry. In this connection, the study of the catalytic properties of rare elements, in particular rhenium, is of great importance. The literature on the catalytic properties of rhenium is very small in volume and in the case of the use of rhenium catalysts under pressure is confined to one patent. Platonov and co-workers have prepared active dispersed rhenium catalysts for the hydrogenation of carbon monoxide and ethylene derivatives, and also for the dehydrogenation of alcohols [1-6]. The same author [7] first showed that dispersed rhenium can be used for the dehydrogenation of cyclohexane. In 1958 Balandin and co-workers [8] investigated the kinetics of the dehydrogenation of cyclohexane and showed that the most active catalyst at 360-380° was 30% rhenium-charcoal, over which the yield of benzene was 90-95%. However, the initially high activity of this catalyst fell rapidly after only 5-7 minutes of work. In 1956 there appeared a German Democratic Republic patent [9] which referred to the dehydrogenation of a gasoline fraction (100-180°) containing 14% of aromatic hydrocarbons (octane rating 53) in presence of rhenium on active alumina at 475-500° and 50 atm. As a result of the reforming up to 49% of aromatic hydrocarbons was formed and the octane rating was raised to 71. The patent does not state the method of preparation of this catalyst, but indicates that rhenium catalysts are more effective than platinum catalysts in promoting the isomerization of n-paraffins and their dehydrocyclization.

In view of the above, we considered it to be of interest to study the catalytic properties of rhenium on alumina under the conditions for the reforming of gasoline fractions for the case of individual hydrocarbons. For the present investigation we chose hexane, methylcyclopentane, and cyclohexane. If rhenium catalysts are found to be suitable for the reforming of gasoline fractions, both with the object of obtaining aromatic hydrocarbons and with the object of improving engine-performance properties, they may acquire not only theoretical, but also practical importance.

In the present paper, we studied the catalytic properties of five rhenium catalysts in their relation to the metal content of the catalyst, the presence of zinc oxide or hydrofluoric acid, and the temperature and pressure of the hydrogen. It was shown that catalysts containing 5% and 15% of rhenium on the alumina either do not dehydrogenate cyclohexane, or dehydrogenate it only to a slight extent. A catalyst containing 20% of rhenium on alumina showed very high dehydrogenating power. Over this catalyst at 385° with a hydrogen pressure of 5 atm we succeeded in obtaining yields of up to 80% of benzene. An addition of 5% of zinc oxide to a catalyst consisting of 20% rhenium and 75% of alumina did not result in any change in properties, as compared with a catalyst consisting only of 20% of rhenium and 80% of alumina. Treatment of a catalyst containing 20% of rhenium on alumina with hydrofluoric acid did not increase its isomerizing activity substantially. Rise in temperature (from 300° to 480°), as also rise in pressure (from 5 to 30 atm) led to a considerable increase in the

extent of hydrocracking of the original hydrocarbons. Thus, in the catalytic treatment of hexane over a 20% $Re - Al_2O_3$ catalyst (485°, 30 atm of H_2, space velocity v = 1.0 hr^{-1}, molar ratio of hydrogen to hydrocarbon = = 5) the extent of the hydrocracking of the original hydrocarbon reached about 90%.

Analysis of the gaseous products of the catalysis showed that they consisted of 79% of methane, 3% of ethane, 1.5% of propane, 0.6% of butane, and 0.3% of pentane. Lowering of the experimental temperature, and also of the hydrogen pressure, led to considerable suppression of the hydrocracking of the hydrocarbons investigated. Thus, in the catalytic treatment of cyclohexane, hexane, and methylcyclopentane at 305-400° and 5 atm, with v = 1.0 hr^{-1} and H_2 : hydrocarbon = 5, the extent of hydrocracking was lowered to 8-15%. Of the five catalysts investigated the most active was 20% $Re - Al_2O_3$, with which the dehydrogenation of C_6H_{12} was carried out over a period of 21 hours.

EXPERIMENTAL

For the preparation of the catalysts rhenium was dissolved in 10% nitric acid in a boiling water bath. Alumina, which was first roasted in a muffle furnace at 500° for five hours, was formed into cylinders 5 x 5 mm and impregnated with rhenic acid. The catalyst was dried in a drying oven at 130° for 3-4 hours and reduced with hydrogen for ten hours at 470-480°. In all, five samples of $Re - Al_2O_3$ catalysts were prepared: 1) 5% $Re - Al_2O_3$; 2) 15% $Re - Al_2O_3$; 3) 20% $Re - Al_2O_3$; 4) 20% $Re - Al_2O_3$, 5% ZnO and 75% Al_2O_3; 5) 20% $Re - Al_2O_3$ and 1.2% HF.

The experiments were carried out in a flow-type apparatus [10] at various temperatures (290-480°); the hydrogen pressure was varied from 5 to 30 atm, the space velocity of feed of hydrocarbons was 1.0 hr^{-1}, and the molar ratio of hydrogen to hydrocarbon was maintained at 5 : 1. The charge of reduced catalyst amounted to 30 ml.

The analysis of the catalyzate consisted in determinations of density, refractive index, and content of aromatics (sulfuric acid method). Some catalyzates were subjected to chromatographic separation and also fractionation through a column of 40-plate efficiency. The hydrocarbon compositions of fractions were determined by the method of gas-liquid chromatography. The chromatographic analysis of fractions was carried out at 50° through a column, length 2 m and diameter 0.6 cm, filled with kieselguhr moistened with tritolyl phosphate. As carrier gas we used hydrogen, which was passed at a rate of 30 ml/min at a pressure of 0.18 atm. For the analysis of the gas leaving the column we used a simple microflame detector [11, 12]. The volume of the entering test sample did not exceed 0.01 ml. For the purpose of qualitative analysis we carried out the chromatography of artificial mixtures containing isopentane, pentane, cyclopentane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, hexane, methylcyclopentane, cyclohexane, and benzene. It was shown that the column used effected satisfactory separation of these components with the exception of mixtures of hexane and cyclopentane and also of 2,2-dimethylbutane and 2-methylpentane. These hydrocarbons show a small splitting of the peak only when their concentrations in the mixture are very close. It is noteworthy that 2,2-dimethylbutane and cyclopentane, which have very close boiling points (49.4° and 49.7°, respectively), are separated completely. Comparison of the chromatograms of catalyzate fractions with those of standard mixtures (Fig. 1) determines the qualitative compositions of the fractions unequivocally. As hexane and cyclopentane give a single peak in common on the chromatogram, the question of the predominance of one or other of these in a given fraction was determined on the basis of the boiling point of the fraction. The evaluation of the contents of the individual hydrocarbons in the fractions investigated was made from the chromatogram in the following way. The area of each peak was calculated from the formulas for triangles. When the peak had marked lack of symmetry the area was calculated as the sum of the areas of two or more triangles. The so-calculated areas of all the peaks of the chromatograms were then added together and the area of each peak was related to the sum obtained (Fig. 2).

As the main components of the catalysis products were hexane, methylcyclopentane, and cyclohexane, for the verification of the accuracy of the method we prepared artificial mixtures of these hydrocarbons. The results of the analysis are presented in Table 1. This shows that the analysis is accurate within ± 2.4%. When complete separation of the peaks corresponding to separate hydrocarbons did not occur on the chromatogram, the contour of each peak was continued to the zero line, the area of each peak was calculated, and the relative content of each component in the fraction investigated was calculated as in the case of complete separation (Fig. 2).

Gaseous reaction products were analyzed in a VTI apparatus and on a chromathermograph.

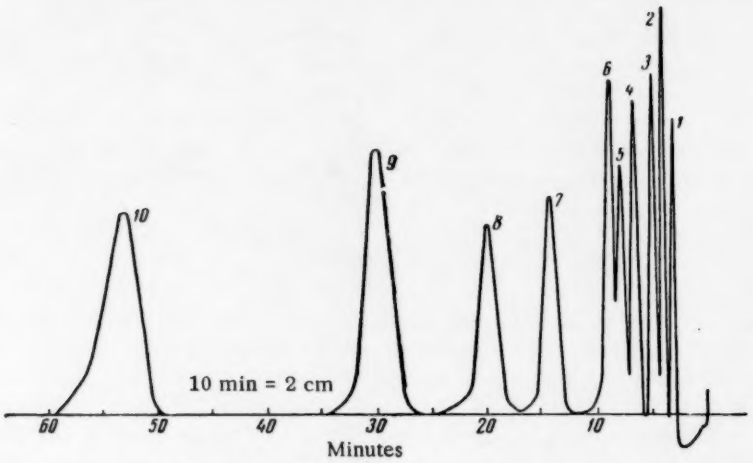


Fig. 1. Chromatogram of artificial mixture of hydrocarbons: 1) isopentane; 2) pentane; 3) 2,2-dimethylbutane; 4) 2,3-dimethylbutane + methylpentane; 5) 3-methylpentane; 6) hexane + cyclopentane; 7) methylcyclopentane; 8) cyclohexane; 9) methylcyclohexane; 10) benzene.

TABLE 1

Accuracy of Method of Chromatographic Analysis (separation of artificial mixtures)

Mixture	Hydrocarbons	Content (% by wt.)		Error in determination (absolute %)
		Actual	Found by analysis	
I	Hexane	33,1	32,5	—0,6
	Methylcyclopentane	34,8	34,4	-—0,4
	Cyclohexane	32,1	33,1	+1,0
II	Hexane	6,4	5,5	+0,9
	Methylcyclopentane	8,9	7,4	—1,5
	Cyclohexane	84,7	87,1	—2,4
III	Hexane	85,0	87,0	+2,0
	Methylcyclopentane	7,0	5,3	—1,7
	Cyclohexane	8,0	7,2	—0,8
IV	Hexane	8,0	8,5	—0,5
	Methylcyclopentane	81,0	81,0	0
	Cyclohexane	11,0	10,4	—0,6
			(Greatest error in determination)	±2,4%

The cyclohexane taken for investigation had b. p. 80.8° (756 mm), $n^{20}D$ 1.4262 and d^{20}_4 0.7782. Methylcyclopentane was prepared by the dehydration and isomerization of cyclohexanol over Al_2O_3 at 450° with v = 0.3 hr^{-1}, subsequent hydrogenation of the unsaturated mixture formed in an autoclave over Raney nickel, and fractionation through a column of 80-plate efficiency. The methylcyclopentane used had b. p. 71.8° (752 mm), $n^{20}D$ 1.4090 and d^{20}_4 0.7487. The hexane used had b. p. 68.5° (754 mm), $n^{20}D$ 1.3750 and d^{20}_4 0.6599.

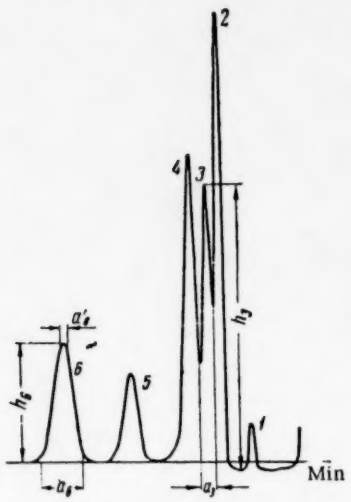
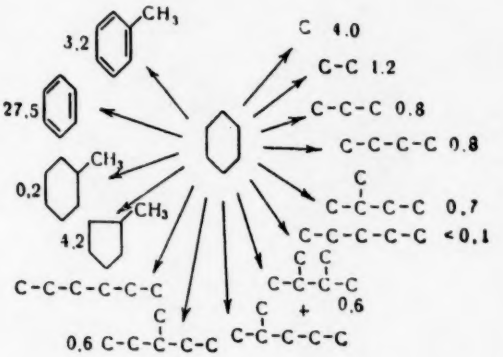


Fig. 2. Chromatogram of Fraction I of cyclohexane catalyzate: 1) pentane; 2) 2,3-dimethylbutane + + 2-methylpentane; 3) 3-methylpentane; 4) cyclopentane; 5) methylcyclopentane; 6) cyclohexane. % of component i = $\frac{s_i}{\sum_{i=1}^{i=6} s_i}$ $s_i = \frac{a_i + a'_i}{2} h_i$; when $a'_i = 0$ $s_i = \frac{a_i \cdot h_i}{2}$

The catalyzates of cyclohexane, hexane, and methylcyclopentane, obtained at 300-385°, under 5 atm, with v = 1.0 hr^{-1}, at H_2:hydrocarbon = 5, over 20% Re – Al_2O_3, were subjected to detailed investigation.

The cyclohexane catalyzate, obtained at 385° in 91% yield and characterized by $n^{20}D$ 1.4460 and d^{20}_4 0.7965 and an aromatics content of 34%, was subjected to chromatographic separation on silica gel. After removal of isopentane by distillation, the paraffin-naphthene part of the catalyzate then separated had $n^{20}D$ 1.4215 and d^{20}_4 0.7661; it was fractionated, and the fractions were then investigated by the method of gas-liquid chromatography. In the aromatic part of the catalyzate we detected benzene (30.3%) and toluene (3.7%). The results of the fractionation of the paraffin-naphthene part of the catalyzate are presented in Table 2. This shows that the paraffin-naphthene part of the catalyzate contained, apart from unchanged cyclohexane, seven hydrocarbons: pentane (0.1%), 2,3-dimethylbutane and 2-methylpentane (0.7%), 3-methylpentane (0.7%), hexane (1.5%), methylcyclopentane (4.6%), and methylcyclohexane (0.2%). In the gaseous catalysis products we found: H_2 – 69.5%, CH_4 – 22.2%, C_2H_6 – 3.7%, C_3H_8 – 1.6%, C_4H_{11} – 1.2% and i-C_5H_{12} – 0.9%.

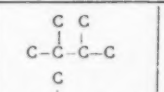
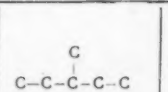
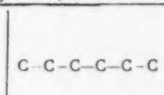
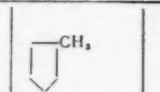
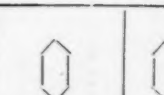
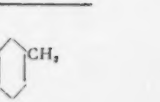
Hence, the transformations of cyclohexane (% by weight on original hydrocarbon) over a 20% Re – Al_2O_3 catalyst may be represented by the following scheme:



In addition to the main dehydrogenation product, benzene, we found methylcyclopentane (about 5%) in the catalyzate, which indicates reaction with ring contraction. The formation of normal and branched paraffins may proceed through the hydrogenolysis of the methylcyclopentane formed. The formation of methylcyclohexane and toluene may be explained as the result of the alkylation of cyclohexane and benzene with methylene radicals arising in the given conditions as a result of methane scission of cycloalkanes, on analogy to the reactions occurring over a platinum-alumina catalyst [13].

TABLE 2

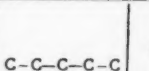
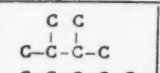
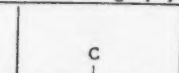
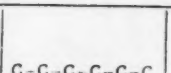
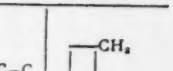
Properties and Composition of the Paraffin-Naphthene Part of the Cyclohexane Catalyzate

Fraction	Boiling range (°C)	Yield (% on C_6H_{12} catalyzate)	Constants		Hydrocarbons determined by gas-liquid chromatography*													
			n_D^{20}	d_4^{20}	C-C-C-C													
					a	b	a	b	a	b	a	b	a	b	a	b	a	b
I	42,5—60	1,4	1,3800	0,6800	1,4	0,1	24,8	0,4	21,2	0,3	26,3	0,4	8,4	0,1	17,9	0,2	—	—
II	60—68	1,6	1,3865	0,6875	1,1	0,1	16,0	0,2	16,3	0,3	30,6	0,5	35,4	0,6	0,7	0,1	—	—
III	68—72	3,0	1,3995	0,7206	0,5	0,1	3,3	0,1	4,9	0,1	21,8	0,6	65,5	2,0	4,0	0,1	—	—
IV	72—79	4,2	1,4175	0,7615	—	—	—	—	—	—	—	—	46,4	1,9	53,6	2,3	—	—
V	79—80	50,1	1,4260	0,7780	—	—	—	—	—	—	—	—	—	—	100,0	50,1	—	—
Residue		4,8	1,4240	—	—	—	—	—	—	—	—	—	—	—	96,8	4,6	3,2	0,2
Losses		0,9	—															
Total		66,0	—	—	—	0,1	—	0,7	—	0,7	—	1,5	—	4,6	—	57,4	—	0,2

* a) Content (%); b) yield (% on cyclohexane catalyzate).

TABLE 3

Properties of Hexane Catalyzate

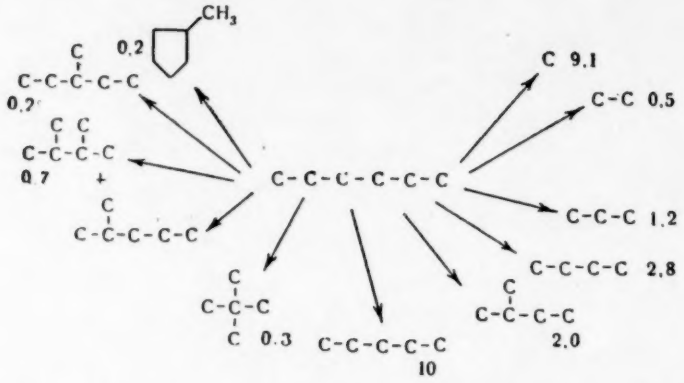
Fraction	Boiling range (°C)	Yield (% on C_6H_{14} catalyzate)	Constants		Hydrocarbons determined by gas-liquid chromatography*													
			n_D^{20}	d_4^{20}														
					a	b	a	b	a	b	a	b	a	b	a	b	a	b
I	32,5—35	6,7	1,3550	0,6219	4,9	0,3	5,6	0,4	89,5	6,0	—	—	—	—	—	—	—	—
II	35—50	5,9	1,3570	0,6244	0,8	<0,1	1,5	<0,1	87,5	5,2	6,6	0,4	—	—	3,6	0,2	—	—
III	50—60	1,5	1,3660	0,6297	—	—	—	—	40,5	0,6	24,5	0,4	12,0	0,2	23,0	0,3	—	—
IV	60—67,5	71,1	1,3740	0,6584	—	—	—	—	—	—	—	—	—	—	100,0	71,1	—	—
Residue		8,8	1,3745	0,6590	—	—	—	—	—	—	—	—	—	—	98,2	8,7	1,8	0,2
Gas from debutanization		4,0																
Losses		2,0																
Total		100,0				0,4		0,5		11,8		0,8		0,2		80,3		0,2

* a) Content (%); b) yield (% on C_6H_{14} catalyzate).

** Identified by the position of the peak on the chromatogram.

The hexane catalyzate, obtained at 300° in 85% yield and characterized by $n^{20}D$ 1.3700 and d^{20}_4 0.6484 (58 ml weighed 37.6 g), was first heated to remove dissolved gaseous catalysis products. In the products separated (about 4%) we found: 1.5% – C_2H_6, 24.7% – C_3H_8, 51.3% – C_4H_{10} and 21.5% – i-C_5H_{12}. The catalyzate was then fractionated; the results are presented in Table 3. This shows that the catalyzate contained about 14% of hydrogenolysis and isomerization products, etc. Thus, apart from unchanged hexane we detected seven hydrocarbons: 2,2-dimethylpropane (0.4%), isopentane (0.5%), pentane (11.8%), 2,3-dimethylbutane and 2-methylpentane (0.8%), 3-methylpentane (0.2%), and methylcyclopentane (0.2%). In the gaseous catalysis products we found: 71% – H_2, 26% – CH_4, 0.6% – C_2H_6, 0.6% – C_3H_8, 0.8% – C_4H_{10} and 0.5% i-C_5H_{12}.

Hence, the transformations of hexane (% on original hydrocarbon) may be represented by the following scheme:



As will be seen for the analysis given for the hexane catalyzate, about 10% of it is accounted for by pentane, but the isomerization of hexane is observed only to a slight extent (about 1%). It is interesting that some methylcyclopentane (about 0.2%) is formed in the catalyzate. The formation of this hydrocarbon is most probably to be attributed to the cyclization of hexane.

The methylcyclopentane catalyzate, obtained at 305° in 85% yield and characterized by $n^{20}D$ 1.4065 and d^{20}_4 0.7295 (117 ml weighed 85.5 g), was first heated to remove dissolved gaseous catalysis products. In the products isolated (about 18%) we found: 3.1% – C_2H_6, 20.3% – C_3H_8, 51% – C_4H_{10} and 25.6% – i-C_5H_{12}. The catalyzate was then fractionated. The results are presented in Table 4. This shows that methylcyclopentane undergoes a variety of transformations. Thus, apart from methylcyclopentane, in the catalysis products we detected nine hydrocarbons: 2,2-dimethylpropane (0.2%), isopentane (2.1%), pentane (1.8%), 2,3-dimethylbutane and 2-methylpentane (3.8%), 3-methylpentane (4.7%), hexane (0.5%), cyclopentane (1.5%), and cyclohexane (1.4%). In the gaseous catalysis products we found: 67.5% – H_2, 26.2% – CH_4, 3.4% – C_2H_6, 1.5% – C_3H_8, 0.9% – C_4H_{10} and 0.5% – i-C_5H_{12}.

Hence, the transformations of methylcyclopentane can be represented by the following scheme:

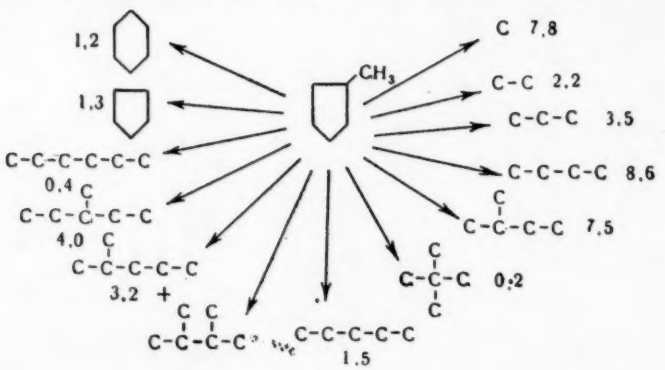
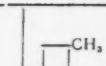


TABLE 4

Properties of Methylcyclopentane Catalyzate

Fraction	Boiling range (°C)	Yield (% on methylcyclopentane catalyzate)	Constants		Hydrocarbons determined by gas-liquid chromatography*																	
			n_D^{20}	d_4^{20}	C•• / C–C–C / C		C / C–C–C–C		C C C C		C C / C–C–C–C / C / C–C–C–C		C / C–C–C–C–C		C–C–C C–C–C							
					a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b
I	25,5—31	2,8	1,3535	0,6183	5,5	0,2	60,2	1,7	34,3	1,0	—	—	—	—	—	—	—	—	—	—	—	—
II	31—51	2,6	1,3775	0,6696	0,2	<0,1	14,2	0,4	32,5	0,8	15,6	0,4	—	—	—	—	37,5	1,0	—	—	—	—
III	51—61	4,4	1,3765	0,6658	—	—	0,5	<0,1	0,5	<0,1	46,6	2,0	39,0	1,7	—	—	12,3	0,5	1,1	<0,1	—	—
IV	61—70	5,5	1,3795	0,6670	—	—	—	—	—	—	24,6	1,4	53,8	3,0	9,9	0,5	—	—	11,7	0,7	—	—
V	70—72	59,5	1,4090	0,6670	—	—	—	—	—	—	—	—	—	—	—	—	—	—	100	59,5	—	—
Residue•••		5,2	1,4190	0,7486	—	—	—	—	—	—	—	—	—	—	—	—	—	—	64,7	3,3	27,0	1,4
Gas from debutanization		18,0																				
Losses		2,4																				
Total		100				0,2		2,1		1,8		3,8		4,7		0,5		1,5		63,6		1,4

* a) Content (%); b) yield (% on methylcyclopentane catalyzate).

** Identified by the position of the peak on the chromatogram.

*** In the residue we detected 0.4% of a hydrocarbon of composition higher than cyclohexane, but we did not identify it.

The formation of cyclohexane in the catalyzate can be explained by the enlargement of the five-membered ring into a six-membered. As a result of the hydrogenolysis of the methyl group of methylcyclopentane, cyclopentane, its hydrogenolysis product pentane, and also the isomerization product of the latter, 2-methylbutane, are formed in the catalyzate. As well as these reactions there occurs the hydrogenolysis of the methylcyclopentane ring with formation of hexane and its isomers.

SUMMARY

1. A study was made of the catalytic properties of five rhenium-alumina catalysts of different rhenium contents (5, 15, and 20%) and with additions of ZnO and HF; they were used in the treatment of cyclohexane, hexane, and methylcyclopentane at 290-480° in presence of hydrogen at 5-30 atm at a space velocity of 1.0 hr^{-1} and a hydrogen to hydrocarbon ratio of 5.

2. Under the conditions investigated aromatic hydrocarbons (up to 78%) were formed only from cyclohexane. At temperatures above 400° and hydrogen pressures of 20 and 30 atm much hydrocracking of hydrocarbons was observed (about 60%). Hexane gave a particularly large amount of hydrocracking (up to 90%).

3. The most active catalyst found for the dehydrogenation of cyclohexane (380°, 5 atm), the hydrogenolysis of hexane (300°, 5 atm), and the hydrogenolysis of methylcyclopentane (305°, 5 atm) was 20% $Re - Al_2O_3$.

4. The catalyzates of cyclohexane, hexane, and methylcyclopentane were subjected to detailed investigation by gas-liquid chromatography.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

HYDROGENATION OF DI-2-CYCLOPENTEN-1-YLACETYLENE OVER Pd, Pt, AND Ni CATALYSTS

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No. 8, pp. 1481-1489, August, 1960
Original article submitted March 7, 1959

From the investigation of Zal'kind [1], Bourguel [2], and other [3-5], who studied the hydrogenation of phenyl- and diphenyl-acetylenes, it follows that palladium brings about the selective hydrogenation of the triple bond to a double bond. Other authors, who worked with acetylene itself and its derivatives, confirmed this and showed that only after the disappearance of the triple bond does hydrogenation of the double bond begin. Dupont [6] found that Raney nickel also shows selectivity toward an acetylenic bond. Platinum catalysts are less selective. Thus, after the addition of two atomic proportions of hydrogen to phenylacetylene in presence of a palladium catalyst no acetylenic carbon could be detected in the reaction mixture, whereas in presence of a platinum catalyst its presence could still be detected [7].

The hydrogenation of monoethylenic hydrocarbons has been studied in great detail. As a result of an investigation of the rate curves for the addition of hydrogen to numerous aliphatic hydrocarbons Lebedev and co-workers [8] showed that the degree of substitution of the hydrogen atoms at a double bond affects the hydrogenation process. It was shown that monosubstituted ethylene derivatives have the greatest and tetrasubstituted derivatives have the least rates of addition of hydrogen; di- and tri- substituted ethylenic hydrocarbons occupy an intermediate position. The authors advanced the view that this rule is observed also in the hydrogenation of mixtures of hydrocarbons with varying degrees of substitution of carbon atoms linked by a double bond.

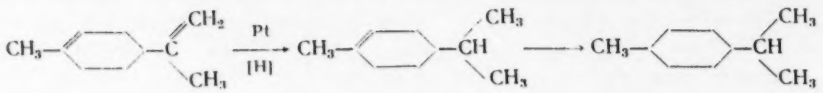
Lebedev and Platonov [9], in a study of the hydrogenation of cyclohexenes, extended to these the rule already established for aliphatic compounds; they showed also that on addition of hydrogen to mixtures of unsaturated hydrocarbons in presence of platinum black alicyclic and acyclic ethylene derivatives of identical degree of substitution behave differently, and the difference between them becomes more marked in the case of tri- and tetrasubstituted ethylenes. Disubstituted cyclic ethylenes, i.e. cyclic hydrocarbons having no substituents at the double bond, and disubstituted ethylenes with an open chain are hydrogenated simultaneously, whereas trisubstituted ethylenes with an open chain are hydrogenated before cyclic trisubstituted ethylenes. However, these conclusions of Lebedev and Platonov cannot be regarded as completely proved since no proofs other than rate curves for the absorption of hydrogen were advanced in their favor.

Moreover, in a study of the literature on this question the lack of justification of some of the comparisons becomes obvious, e.g. comparisons of the rate of the addition of hydrogen to olefins, on the one hand, and to unsaturated functional derivatives, on the other. Particularly cautious treatment must be given to conclusions drawn about the direction of the addition of hydrogen to ethylenic hydrocarbons in presence of palladium catalysts, since for a long time due attention was not given to the isomerizing properties of this catalyst. Kazanskii, Lukina, Malyshev, and others [10], in a study of the partial (to the extent of 20%) addition of hydrogen to 2-methyl-1-pentene and 2-methyl-2-pentene in an alcoholic medium at room tempterature and atmospheric pressure, showed that in presence of palladium the isomerization of these hydrocarbons occurred with formation of an equilibrium mixture, whereas in presence of platinum [11] such isomerization did not occur.

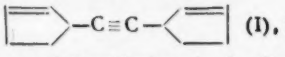
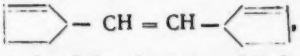
Gostunskaya, Dobroserdova, and Kazanskii [12], for the case of isoamylenes and 2,5-dimethyl-3-hexene, also observed that in presence of platinum only addition of hydrogen occurred, where as in presence of palladium with partial addition of hydrogen there was simultaneous isomerization with displacement of the double bond. Results obtained on the isomerizing action of palladium under mild conditions of catalytic hydrogenation compels one to make a reexamination of some conclusions reached earlier on the selective action of various catalysts in the addition of hydrogen to unsaturated compounds.

The question of the direction of the addition of hydrogen to di- and poly-olefins, in which the double bonds may be isolated, conjugated, or cumulative, is still more complex. The most detailed study has been given to the hydrogenation of aliphatic hydrocarbons having a system of conjugated double bonds. It was here shown that first one and then the other molecule of hydrogen may add successively at different rates, or both molecules of hydrogen may occur in all possible directions, depending both on the character of the substitution at the doubled-bonded atoms and on the nature of the catalysts and solvents.

The hydrogenation of hydrocarbons containing several isolated double bonds has received relatively little study. It is known that in individual cases such hydrocarbons may undergo selective hydrogenation, and in some cases Lebedev's rule has been confirmed. Vavon [13] was the first to observe that in the hydrogenation of limonene in presence of platinum black the two molecules of hydrogen add at different rates: the first more rapidly than the second. Here the isopropenyl group (disubstituted ethylene) is hydrogenated first, and onlv after the addition of one molecule of hydrogen does the second double bond (trisubstituted bond in the ring) begin to be hydrogenated:

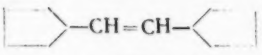


Such selectivity in the addition of hydrogen to limonene was observed also by Ipat'ev [14] in hydrogenation over copper catalysts under pressure and by Armstrong and Hilditch [15] over nickel. On the other hand, in the hydrogenation of 1,5-dimethyl-1,5-hexadiene [8] in presence of platinum no selectivity was observed: the two molecules of hydrogen added at equal and constant speeds.

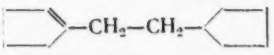
We considered it to be of interest to study the order of the addition of hydrogen to multiple bonds in the case of a compound in which the degree of substitution at the double-bonded carbon atoms was the same in every case, but the bonds differed in that two were present in five-membered rings and one in an aliphatic chain. With this object we studied the hydrogenation of a compound containing two double bonds in five-membered rings and one triple bond between the rings, namely di-2-cyclopenten-1-ylacetylene  (I), in presence of various catalysts; on partial selective addition of hydrogen this compound should give, in the first place, a hydrocarbon with three isolated double bonds  , which is the compound in which we were interested from the point of view of the study of the character of its hydrogenation.

DISCUSSION OF EXPERIMENTAL RESULTS

The rate curves for the addition of hydrogen to di-2-cyclopenten-1-ylacetylene in presence of various catalysts are given in Fig. 1. It will be seen that in presence of platinum the rate of addition of hydrogen remains constant until 75-78% of the hydrogen theoretically required for the complete saturation of the multiple bonds has added. We studied the incomplete-hydrogenation product obtained after the addition of 75% of the hydrogen. It was found that it did not contain compounds with a triple bond and was mainly cis-1,2-dicyclopentylethylene (II)



(II)



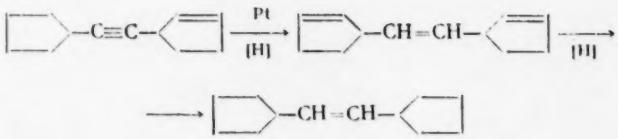
(III)

This conclusion was reached with reasonable certainty on the basis of the Raman spectrum of the catalyzate; in the region of the valence vibrations of the double bond in this spectrum there was only one line, 1651 cm^{-1}, which is characteristic of a cis-disubstituted double bond [16]*. This line might correspond also to 1-(1-cyclo-

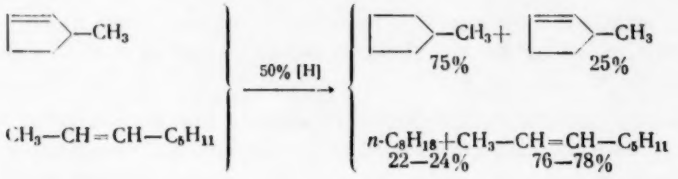
*Here we assume that the frequency of the line does not change on replacement of alkyl groups at the double bond by cyclopentyl groups.

penten-1-yl)-2-cyclopentylethane (III) but, as under the given hydrogenation conditions platinum has no isomerizing action on unsaturated hydrocarbons [11] and compound (III) could not be formed by the direct addition of hydrogen to (I), we reject this possibility. An analysis of the Raman spectra leads to the same conclusion, for in the spectrum of a compound having the structure (III) the presence of lines in the region 800-900 cm^{-1} would be expected (apart from the lines for the pulsation vibration of the five-membered ring), but such lines are not found in the spectrum of the catalyzate.

Hence, in the partial addition of hydrogen to di-2-cyclopenten-1-yl-acetylene in presence of platinum black the double bonds in the five-membered rings appear to be saturated in preference to the aliphatic double bond formed as a result of the partial selective hydrogenation of the triple bond; hence, the addition of hydrogen proceeds in accordance with the scheme:



Since, in the given example in presence of platinum, hydrogen added preferentially to the double bonds in five-membered rings, we considered it to be of interest to study the partial addition of hydrogen to a mixture of two unsaturated hydrocarbons, namely an aliphatic olefin and a cyclopentene homolog in which the degree of substitution at the carbon atoms of the double bond was the same in each case. For this purpose we took an equimolecular mixture of 3-methylcyclopentene and 2-octene. A study of the catalyzate obtained after the addition of 50% of the hydrogen required for the complete saturation of the double bonds in presence of platinum black showed that in this case also there was preferential hydrogenation of the double bond in the five-membered ring: the first hydrocarbon was hydrogenated to the extent of 75%, but the second only to the extent of 22-24%.



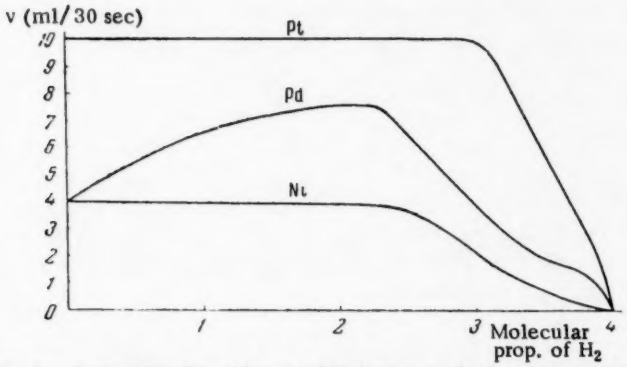
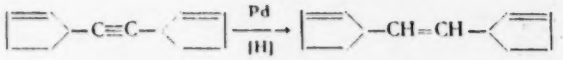


Fig. 1. Curves for the addition of hydrogen to di-2-cyclopenten-1-ylacetylene.

In the presence of palladium black the addition of hydrogen to di-2-cyclopenten-1-ylacetylene proceeded differently. The relevant curve (Fig. 1) shows that the rate of addition of hydrogen at first increases continuously and then, after a maximum is reached (at the absorption of 56-57% of the theoretically required hydrogen), it gradually falls.

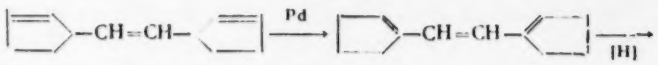
A study of the catalyzate obtained after the addition of 25% of the hydrogen necessary for the complete saturation of the multiple bonds showed that it boiled over a narrow temperature range, contained none of the original compound, and in the region of the valence vibrations of the double bond in the Raman spectrum had

two lines at 1611 and 1649 cm^{-1} of approximately equal intensity. The first corresponded to the double bond in a five-membered ring (having no substituents on the double- bonded carbons), and the second could correspond to a cis-disubstituted ethylenic bond in an aliphatic chain (see above). In this case the product had the structure of 1,2-di-2-cyclopenten-1-ylethylene (IV), in which there is a system of three isolated double bonds. As isomerization with displacement of double bonds is possible in presence of palladium, we must take into consideration also that the frequency 1649 cm^{-1} may belong to a double bond in a five-membered ring such that there is a substituent on one of the carbon atoms of the double bond. A bond of this kind is present in compounds (V) and (VI), in which, however, the double bonds are conjugated, and it is known that conjugation leads to a considerable increase in the intensity of the frequencies corresponding to the double bonds, which is not observed in the case of the catalyzate under investigation. We may therefore conclude that the addition of 25% of hydrogen proceeds according to the scheme

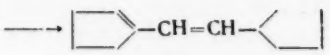


(IV)

and that isomerization with displacement of the double bonds proceeds only to a slight extent, if at all:



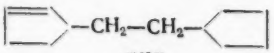
(IV) (V)



(VI)

Hence, while the mixture still contains some of the original compound with a triple bond the isomerizing action of palladium scarcely shows itself because of the preferential absorption of molecules on the catalyst at the C ≡ C bond.

However, with the further addition of hydrogen (hydrogenation to the extent of 75%) in presence of palladium the picture becomes complicated and there appears to occur considerable isomerization with displacement of double bonds. In the spectrum of the resulting catalyzate in the region of the valence vibrations of the double bond there are three lines: 1617 (1), 1652 (9), and 1678 (3) cm^{-1}. The first (the weakest) appears to correspond to 1-(2-cyclopenten-1-yl)-2-cyclopentylethane (VII)



(VII)

and the second, the most intense, may be attributed, with equal justification, to cis-1,2-dicyclopentylethylene (II) and 1-(1-cyclopenten-1-yl)-2-cyclopentylethane (III). We succeeded in proving the presence of these two compounds experimentally by a study of the products of the oxidation of the catalyzate with potassium permanganate, as a result of which we isolated cyclopentanecarboxylic acid

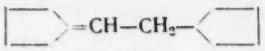
(II)

and 7-cyclopentyl-5-oxoheptanoic acid

(III)

No other oxidation products were detected.

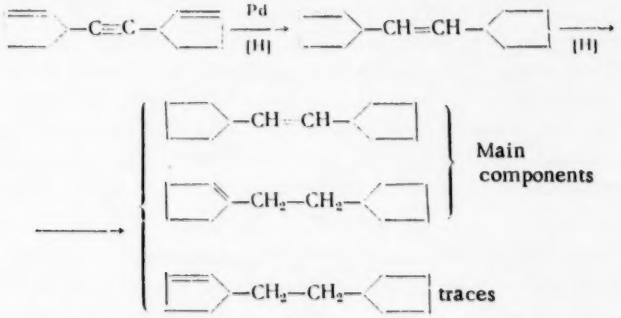
The line 1678 cm^{-1} may belong to trans-1,2-dicyclopentylethylene (II), for according to Goubeau [16] trans-disubstituted ethylenes in the aliphatic series correspond to a frequency of 1670-1673 cm^{-1}; this frequency may correspond also to 1-cyclopentyl-2-cyclopentylideneethane (VIII)



(VIII)

for it has been shown recently [17] that the double-bond frequency in the spectra of ethylidene-, propylidene- and butylidene-cyclopentanes is 1680-1681 cm^{-1}. However, on oxidation of (VIII) with potassium permanganate cyclopentanone should be formed, and we could not detect this in the oxidation products of the catalyzate. Hence, while not rejecting finally the possibility that such a compound is present in the catalyzate in small amounts, we are more inclined to attribute the frequency of 1678 cm^{-1} to trans-1,2- dicyclopentylethylene (II), by the oxidation of which cyclopentanecarboxylic acid is again formed*.

Hence, in the 75% hydrogenation of di-2-cyclopenten-1-ylacetylene in presence of palladium, the mixture formed is more complex than that formed in presence of platinum and its main components are dicyclopentylethylene (II) and 1-(1-cyclopenten-1-yl)-2-cyclopentylethane (VII). The formation of these and other hydrocarbons may be the result of several reactions: the hydrogenation and isomerization of substances formed at different stages of the hydrogenation (addition of the first, second, and third molecule of hydrogen):



As regards the addition of hydrogen to di-2-cyclopenten-1-ylacetylene in presence of Raney nickel, as can be seen from Fig. 1 in this process there first occurs absorption of hydrogen at a uniform rate and, after the absorption of two molecular proportion of hydrogen, the rate of hydrogenation slowly falls. On fractional distillation of the catalyzate obtained as a result of the addition of 75% of the total hydrogen required, it was found that no single component was present in predominant amount and that the mixture formed boiled over a wide temperature range. We did not study this mixture in greater detail.

From the present investigation it may be concluded that the presence in a molecule of not only a triple bond, but also double bonds in five-membered rings, does not hinder the selective hydrogenation of the triple bond in presence of palladium, because the molecule appears to be preferentially absorbed on the catalyst at the triple bond. To Lebedev's rules on the relation of the rate of addition of hydrogen to double bonds in presence of platinum to the number of substituents at the double bond we can make this supplement: for a given degree of substitution at a double bond in presence of platinum the double bond in a five-membered ring is hydrogenated preferentially to a double bond in an open chain. However, on hydrogenation in presence of palladium the isomerizing action of the latter results in the formation of a mixture of products; a similar picture, with the formation of a still more complex mixture, is observed also in presence of nickel.

EXPERIMENTAL

Di-2-cyclopenten-1-ylacetylene (I) was prepared by the reaction of the Iotsich complex with 2-cyclopen-

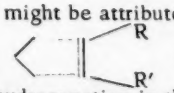
*A frequency of 1678 cm^{-1} might be attributed also to a cyclopentene in which there is a substituent on each of the double bonded atoms:  However, it can scarcely be imagined that skeletal isomerization of this kind could occur in hydrogenation in the cold in the presence of palladium.

TABLE 1

Hydrogenation of Di-2-cyclopenten-1-ylacetylene

Expt.	Amt. taken for reaction			Consumption of hydrogen			Notes
	Dicyclopentenylacetylene (g)	Alcohol (ml)	Catalyst (g)	(moles)	(ml of STP) Theoretical	(ml of STP) Exptl.	
1	0,4003	40	Pt 0,20	4	227	229	Bend after addition of 75% H_2
2	0,2387	30	Pt 0,087	4	163	164	Bend after addition of 78% H_2
3	25,1	100	Pt 1,2	3	10670		
4	0,3298	30	Pd 0,067	4	187	181	Maximum after addition of 57% H_2
5	0,3378	30	Pd 0,067	4	191	186	Maximum after addition of 56% H_2
6	12,33	50	Pd 0,51	1	1750	1760	
7	17,2	50	Pd 0,60	3	7310	7330	
8	0,30	30	Ni 0,30	4	170	173	
9	10,0	50	Ni 3,0	3	4250	4280	

ten-1-yl chloride [18]; it has: b.p. 106° (9–9.5 mm); n_D^{20} 1.5172; d_4^{20} 0.9596. The hydrogenation was carried out in glass hydrogenation flasks at room temperature and atmospheric pressure; agitation was effected by means of a shaker giving 150-180 double shakes per minute. The rate of absorption of hydrogen was determined every 30 seconds with the aid of a gas buret having 1-ml graduations. A fresh portion of catalyst was taken for each experiment. Platinum and palladium blacks were prepared by Zelinskii's method [19] and Raney nickel by Adkin's method [20]. The experimental results are given in the table; curves were constructed from the results of Experiments 1, 2, 4, and 8 (Fig. 1).

In the investigation of the reaction products alcohol was washed from the catalyzate with water, and the catalyzate was then dried with calcium chloride and distilled through a column of 40-plate efficiency. Catalyzate of Expt. 3: Fraction I, head fraction up to 90.2° (7 mm), 1 g (n_D^{20} 1.4804); Fraction II, b.p. 90.2-90.4° (7-7.5 mm), 14.8 g (n_D^{20} 1.4822); Fraction III, residue from distillation, 5 g (n_D^{20} 1.4864).

In the Raman spectrum of Fraction II (d_4^{20} 0.8746) only one line, 1651 cm^{-1}, was found in the region of the valence vibrations of the double bond.

Catalyst of Expt. 6. After fractionation we obtained 9.8g; b.p. 99-99.5° (15 mm); n_D^{20} 1.5112; d_4^{20} 0.9061. In the spectrum of this fraction we found bright lines of approximately equal intensity at 1611 and 1649 cm^{-1}.

Catalyst of Expt. 7. Fractionation gave 14.6 g (91% of amount taken in fractionation) of a fraction having b.p. 108-108.5° (13 mm); n_D^{20} 1.4781; d_4^{20} 0.8771. In the spectrum of this fraction we found the lines: 1617(1), 1652(9), and 1678(3) cm^{-1} (the figures in parentheses are visual intensities on a ten-grade scale). On oxidation of the catalyzate of Expt. 7 (3 g) with potassium permanganate (7.5 g) in aqueous solution (120 ml) at 0-5° we obtained about 0.5 g of cyclopentanecarboxylic acid, the amide of which had m.p. 176.5-177° (the literature [21] gives m.p. 179°), and 7-cyclopentyl-5-oxoheptanoic acid, the semicarbazone of which had m.p. 150-151°. Analysis of semicarbazone: Found C 58.10, 58.07; H 8.51; 8.59; N 15.02; 15.10%. $C_{13}H_{23}O_3N_3$. Calculated: C 57.98; H 8.58; N 15.61%.

The catalyzate of Expt. 9 boiled in the range 92.5-98° (9.5 mm) and was not investigated more closely.

Hydrogenation of an Equimolecular Mixture of 2-Octene and 3-Methylcyclopentene over Platinum Black. 2-Octene was isolated by fractionation through a column of 100-plate efficiency from a mixture of octenes obtained by the dehydration of octanol with 2.85% phosphoric acid [22]; it had: b. p. 126.0° (752 mm); n_D^{20} 1.4150. The literature [23] gives: cis-2-octene, b. p. 125.64°, n_D^{20} 1.4150; trans-2-octene, b.p. 125.0°, n_D^{20} 1.4132. 3-Methylcyclopentene was isolated by fractionation through a column of 60-plate efficiency from the mixture of methylcyclopentenes obtained by the isomerization of cyclohexene over alumina; it had: b.p. 64.9° (760 mm) n_D^{20} 1.4219; d_4^{20} 0.7647. The literature [23] gives: b.p. 65.0°; n_D^{20} 1.4207; d_4^{20} 0.7622.

In presence of 0.3 g of platinum black, 2.44 liters (at 19° and 745 mm) of hydrogen (50% of the amount required to saturate the multiple bonds completely) was caused to add to a mixture of 11.2 g (0.1 mole) of 2-octene and 8.2 g (0.1 mole) of 3-methylcyclopentene in 50 ml of alcohol. After suitable treatment the catalyzate was fractionated through a column of 40-plate efficiency.

Fraction I; b.p. 67.7-71.0°; n_D^{20} 1.4162; d_4^{20} 0.7566; 2.1 g; Fraction II; b.p. 71.0°, n_D^{20} 1.4101; d_4^{20} 0.7502; 4.2 g; Fraction III; b.p. 71.0-122°; 1.1 g; Fraction IV; b.p. 122-122.5°; n_D^{20} 1.4112; d_4^{20} 0.7160; 7.2 g; Residue; n_D^{20} 1.4102; 2.0 g.

Fraction I was a mixture of 3-methylcyclopentene and methylcyclopentanes (compostion of mixture, calculated from the additivity of refractive indices and specific volumes: 59% and 41%); Fraction II was almost pure methylcyclopentane; Fraction III was an intermediate fraction; Fraction IV was a mixture of octenes and octane [bromine value 108 (duplicate 111), according to which the octene content of this fraction was 76-77.5%]. Hence, from the results obtained it follows that 3-methylcyclopentene was hydrogenated to the extent of 75%, but 2-octene only to the extent of 22.5-24%.

The spectrum investigations on the catalyzates were carried out in the laboratory of the Spectroscopy Commission of the Academy of Sciences of the USSR by V. T. Aleksanyan and Kh. E. Sterin and in the P. N. Lebedev Physics Institute of the Academy of Sciences of the USSR by M. M. Sushinskii; we express our deep gratitude to these workers.

SUMMARY

1. The presence of palladium the triple C≡C bond in di-2-cyclopenten-1-ylacetylene is selectively hydrogenated to a double bond.

2. In presence of platinum, after the addition of three molecular proportions of hydrogen to di-2-cyclopenten-1-ylacetylene 1,2-dicyclopentylethylene is formed, i.e., the double bonds in the five-membered rings are preferentially hydrogenated.

3. In presence of palladium, as a result of the isomerizing action of this catalyst, the addition of three molecular proportions of hydrogen to di-2-cyclopenten-1-ylacetylene results in the formation of a mixture of unsaturated hydrocarbons, in which 1,2-dicyclopentylethylene and 1-(1-cyclopenten-1-yl)-2-cyclopentylethane predominate.

4. The preferential addition of hydrogen at the double bond in the five-membered ring rather than at the double bond in the open chain is observed also in the partial hydrogenation (to the extent of 50%) of an equimolecular mixture of 3-methylcyclopentene and 2- octene over platinum black.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

HIGH-TEMPERATURE DEHYDROGENATION OF ETHYLBENZENE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
No. 8, pp. 1490-1494, August, 1960
Original article submitted March 16, 1959

This paper describes an investigation of the kinetics of the dehydrogenation of ethylbenzene at 660-740°. Apart from general interest, the determination of the kinetic characteristics of the dehydrogenation of ethylbenzene at high temperatures is of considerable importance in the establishment of the laws controlling the formation of styrene compounds in the high-temperature treatment of petroleum products [1]. In the production of olefins and gasoline distillates the formation of styrene compounds in such a treatment is harmful. On the other hand, it is of interest to determine the possibility of obtaining styrene and indene as the desired products by high-temperature methods. It should be noted that the available data [2, 3] on the thermal dehydrogenation of ethylbenzene in the temperature range stated is contradictory, as has been emphasized, particularly in [3]. Remarks made in several articles on the lowering of the yield of styrene in the thermal dehydrogenation with rise in temperature correspond to experiments in which the reaction times were relatively long, whereas for the attainment of high yields rise in temperature must be accompanied by a marked reduction in reaction time.

For reactions of short duration at high temperature means of rapid heating must be arranged. For this reason in our experiments we used a fluid-bed heat-transfer medium which permitted the attainment of a high temperature in a powerful furnace. The use of a fluid bed and a reaction space of special configuration ensured also effective mixing and the establishment of constancy of temperatures and concentrations in the reaction zone. These circumstances greatly facilitated the treatment of the experimental results and, in particular, in this treatment they enabled us largely to exclude the effect of side cracking reaction with formation of benzene and toluene in the calculation of the formal dehydrogenation constant. It should be noted that the general scheme of the performance and treatment of experiments was in many respects analogous to that used by us previously [4].

The experimental arrangement is shown in principle in Fig. 1. The main heating unit was a powerful furnace with a graphite spiral, through which an electric current was passed. We gave a detailed description of a similar furnace in [5], but in the present case the stream of vapor was passed into the reaction tube from below through a special turbulence-promoting sieve. The heat-transference medium (powdered coke having particles of effective diameter 0.1-0.5 mm) was disposed on this sieve. About 50 cc of coke was taken. The diameter of the reaction tube was 40 mm, and the height of the fluid bed of coke had about the same value; such a ratio of the diameter of the layer to its height facilitated mixing. Above the fluid bed carbon dioxide was passed into the tube into the vapor stream to give rapid cooling and dilution of the products in the ratio of about 5 : 1. A special check was made to make sure that no carbon dioxide entered the fluid bed from above. The original ethylbenzene was passed into the reactor at constant rate by means of a spray, the head of which was subjected to uniform pressure from a descending weight with a suspension system linked through toothed gear wheels to the axis of a Warren motor. The experiments were carried out with dilution of the starting material with different proportions of carbon dioxide or, in some cases, nitrogen. The diluting gas was introduced into the ethylbenzene stream before the heater, in which the material was heated to 400° (see Fig. 1). From the heater the vapor was passed to the reactor. The temperature in the reactor was measured with an open platinum/platinum-rhodium thermocouple. At the beginning of the experiment the vapor leaving the reactor was passed into a "blank" line; after the establishment of a stationary state the blank line was shut off by a rapid turn of the tap and the vapor

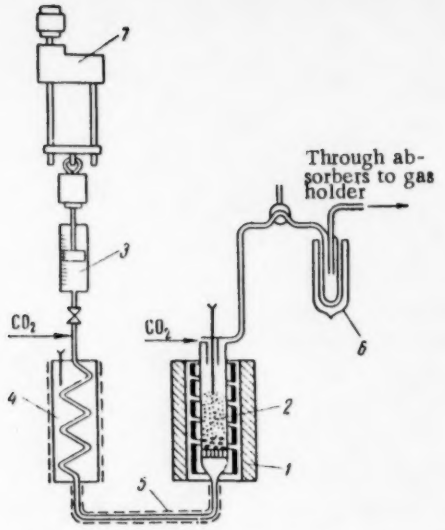

Fig. 1. Experimental arrangement: 1) heating element; 2) fluid bed of heat-transfer medium; 3) buret containing starting material; 4) and 5) heaters; 6) trap; 7) mechanical compressor.

passed into the working system of traps cooled with liquid nitrogen. The gas holder was attached to the line of traps as a reservoir maintaining constant atmospheric pressure at the exit of the reaction system. At the end of the experiment the feed of material was stopped and the system of traps was shut off. The duration of an experiment was 8-10 minutes. The gases condensed in the traps were liberated by warmth and collected in the gas holder.

The distillate formed was weighed, and a determination was then made of its iodine value, which indicated the amount of styrene formed. Also, the distillate was fractionated through a precision vacuum column to determine the amounts of benzene and toluene formed. Apart from individual extremely severe experiments, the yields of distillate were in all cases 90-95% on the weight of the original ethylbenzene. In a control experiment carried out at a reactor temperature of 300° the yield of distillate was 96%. In Table 1 we give the styrene contents of distillate in a series of experiments carried out at 660°, 690°, 720°, and 740° at different dilutions with carbon dioxide. In the third column of the table there are values of τ given by

$$\tau = \frac{V \cdot 0{,}5}{\omega}, \qquad (1)$$

in which ω is the space velocity of the raw material and carbon dioxide at the temperature of the experiment, V is the volume of the reaction zone, and the coefficient 0.5 is the assumed value of the fraction of free volume (porosity of catalyst layer).

The results of the fractionation of the distillate (690° and 720° experiments) with checks on the refractive indices of the fractions showed that it contained 1-5% of benzene and toluene. In the more severe experiments at 740° this value rose to 8-10%. Hence, the predominant process under the conditions described is not cracking, but dehydrogenation*. The yield of styrene on the ethylbenzene that reacted, at maximum absolute yield of styrene, was 58% at 660° and about 70-75% at 690°, 720°, and 740°. Special experiments were carried out to check the possibility that coke had a catalytic action under the conditions investigated. For this purpose the powdered coke used as heat-transfer medium was replaced by ground quartz. The compositions of the liquid products then obtained coincided within the limits of the errors of analysis with those of products obtained over coke at all four of the temperatures investigated.

We will pass to the treatment of the experimental results. Let us denote molar concentrations in the vapor in the reaction zone for ethylbenzene, styrene, toluene, benzene, and carbon dioxide as (C_8H_{10}), (C_8H_8), (C_7H_8), (C_6H_6) and (CO_2) respectively. As the reaction is carried out under conditions of complete mixing, if the dehydration is a first-order process**,

$$(C_8H_8) = k\frac{t}{\alpha}(C_8H_{10}), \qquad (2)$$

*To determine the composition of the gases the process was carried out with dilution of the raw material with nitrogen, instead of carbon dioxide, at 720°. It was shown in these experiments that the volume ratio of methane to hydrogen was about 1:10. It was difficult to determine this ratio accurately because of the great dilution of the gases with nitrogen. Whether the dilution was with carbon dioxide or with nitrogen the composition of the liquid products was the same within the limits of the errors of analysis.

**In our case the process was carried out under conditions remote from those for the attainment of equilibrium concentrations [6], so that the reverse reaction may be neglected.

in which k is the required rate constant for thermal dehydrogenation and α is the coefficient of thermal expansion of the vapor, which determines the increase in volume in the reaction.

It is not difficult to show that in the dehydrogenation reaction

$$\alpha = \frac{1}{1+\dfrac{\pi}{1+\dfrac{[CO_2]_0}{[C_8H_{10}]_0}}} \qquad (3)$$

in which π is the experimentally determinable fraction of styrene in the distillate (see Table 1)

$$\pi = \frac{(C_8H_8)}{(C_8H_{10})+(C_8H_8)+(C_7H_8)+(C_6H_6)} \approx \frac{(C_8H_8)}{(C_8H_{10})+(C_8H_8)} \qquad (4)$$

and subscript zero denotes the initial value. Because of the great dilution, in our experiments the value of α was almost always close to unity. From (2) and (4) we have

$$\pi = \frac{k\dfrac{t}{\alpha}}{1+k\dfrac{t}{\alpha}} . \qquad (5)$$

Transforming (5) further into a form more convenient for treatment, we find

$$\frac{1}{1-\pi} = 1+k\frac{t}{\alpha} . \qquad (6)$$

TABLE 1

Temp. (°C)	Molar dilution C_8H_{10}: CO_2	Time τ sec	Yield of styrene (100 π) (% by vol. on distillate)
660	1 : 1,5	0,663	18,7
	1 : 1,7	0,586	18,4
	1 : 2	0,538	15,7
	1 : 2,1	0,525	13,1
	1 : 2,2	0,507	15,5
	1 : 2,5	0,468	11,9
	1 : 2,8	0,430	13,2
	1 : 3,0	0,412	12,7
	1 : 3,1	0,390	12,9
	1 : 3,5	0,370	8,9
	1 : 3,9	0,339	10,1
690	1 : 1,5	0,590	28,0
	1 : 2,0	0,505	26,8
	1 : 2,1	0,490	25,6
	1 : 2,5	0,440	23,0
	1 : 2,7	0,416	24,7
	1 : 3	0,389	23,3
	1 : 3,5	0,346	25,6
720	1 : 1,5	0,564	34,0
	1 : 1,9	0,497	32,8
	1 : 2,0	0,477	35,4
	1 : 2,1	0,462	35,6
	1 : 2,5	0,417	32,8
	1 : 3,0	0,370	32,6
	1 : 3,5	0,334	30,2
	1 : 3,8	0,314	29,1
740	1 : 3,5	0,298	37,7
	1 : 3,6	0,291	38,6
	1 : 3,6	0,290	39,8
	1 : 3,8	0,281	37,0
	1 : 3,9	0,276	35,2

In Fig. 2 we have plotted the experimentally found relation of $\frac{1}{1-\pi}$ to $\tau = t/\alpha$ for sufficiently small conversion at the four temperatures investigated. As will be seen from Fig. 2, the experimental points are grouped around straight lines, except for experiments giving high conversions, in which side reactions and secondary reactions tart to play an important part. The fact that the experimental results are described satisfactorily by Equation (6), which is derived from (2), confirms the assumed first order of the dehydrogenation reaction and also the realization of effective mixing in the reactor. With aid of Fig. 2 unimolecular dehydrogenation constants were calculated by Equation (6) for different temperatures. The values obtained are given in Table 2.

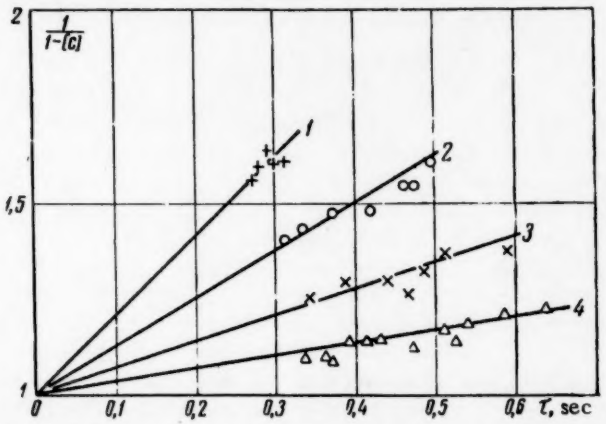

Fig. 2. The relation of 1/1-[c] ([c] = π = styrene content of distillate) to $\tau = t/\alpha$ seconds: 1) 740°; 2) 720°; 3) 690°; 4) 660°.

TABLE 2

Dehydration Constant of Ethylbenzene at Different Temperatures

Temp. (°C)	660	690	720	740
K	0,36	0,70	1,33	2,1

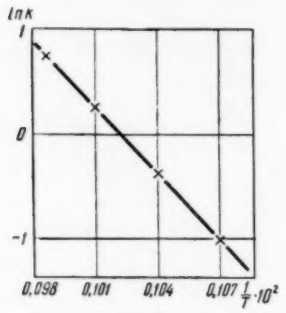

Fig. 3. Relation of ln K to 1/T.

In Fig. 3 we have plotted the relation of ln K to 1/T. Calculation of the activation energy gives 44 ± 2 kcal/mole. This value corresponds to a preexponential factor of about 10^{10}.

In conclusion we may point out that our values of the dehydrogenation constants, associated with relatively low activation energy, are greater than the values of the constants for the over-all thermal transformation of ethylbenzene obtained previously for a similar temperature range by Scwarz [7]. This noncorrespondence is probably associated with the fact that Scwarz's experiments were carried out at very low pressures (a few mm of mercury) and with the fact that in these experiments a method of heating was used which did not ensure a sufficiently rapid establishment of the temperature of the stream of vapor in the reaction tube [8].

SUMMARY

1. The kinetics of the thermal dehydrogenation of ethylbenzene at 660-740° were investigated.

2. The yield of styrene on the ethylbenzene that reacted was 58% at 660° and 70-75% at 690° and 720°.

3. The activation energy for the dehydrogenation of ethylbenzene was calculated; the value obtained was 44 ± 2 kcal/mole.

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CATALYTIC ISOMERIZATION OF CYCLOPROPANE IN MIXTURES WITH OLEFINS

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On examination [1] of the mechanism of the chain heterogeneous catalytic hydropolymerization of olefins under the action of small amounts of carbon monoxide in presence of hydrogen [2], it was noted that there is a tendency for the initiation of the polymerization of olefins by surface alkyl radicals. In this connection it was of interest to determine the properties of linear polymethylene diradicals, particularly the trimethylene diradical in that normal α-olefins absorbed in accordance with Polanyi's scheme do not possess the properties indicated. On the assumption that the trimethylene diradical may be formed as an intermediary in the catalytic isomerization of cyclopropane into propene, in the present work we investigated the effect of additions of cyclopropane to ethylene and propene on the polymerization of the latter in presence of various catalysts. It was found that from the results obtained it was not possible to reach a definite conclusion about the polymerizing effect of an addition of cyclopropane on ethylene and propene because the amount of liquid polymer obtained was always less than corresponded to the amount of cyclopropane that reacted. However, the results enable us to determine the activity of the catalysts used for the isomerization of cyclopropane into a mixture of ethylene and propene. It was found that catalysts containing synthetic aluminum silicate are always active in this reaction, whereas a catalyst for the hydropolymerization of olefins in presence of carbon monoxide (cobalt on clay) showed considerably lower activity.

The isomerization of cyclopropane hydrocarbons under the conditions of heterogeneous catalysis has been studied mainly for substituted cyclopropane [3]; investigations with cyclopropane itself have been very few and have not been in any way concerned with the mechanism of the process. It has been discovered that cyclopropane is isomerized over platinum black very slowly at ordinary temperature, but more rapidly at 100° [4]; the yield of propene at low space velocities is 4-5% at 200° and 29% at 315°; over alumina at 350-385° it is 15-20% [5]. Unlike the catalytic isomerization of cyclopropane, its thermal isomerization, which occurs above 400°, has been studied in greater detail [6], and particular attention has been given to the mechanism of the reaction [7]. In some of these investigation [8, 9] there have been references to the possibility of the intermediate formation of the 1,3-diradical trimethylene, though with the appearance of new work in this field [7, 10] such a reaction mechanism has been placed in doubt.

EXPERIMENTAL

Cyclopropane was synthesized by Gustavson's method [11] by reaction between zinc dust and a 75% alcoholic solution of 1,3-dibromopropane (b.p. 164-167°, d_4^{20} 1.9737; n_D^{20} 1.5228), obtained by the reaction of allyl bromide (b.p. 69-71°; d_4^{20} 1.4335; n_D^{20} 1.4695) with hydrogen bromide in presence of benzoyl peroxide and phosphorus pentoxide with powerful irradiation [12]. In the distillation of the cyclopropane we collected the fraction coming over between −34° and −32°. Ethylene and propene were prepared by the dehydration of ethyl and isopropyl alcohols, respectively, over alumina.

For the quantitative determination of mixtures of propene and cyclopropane we used a method based on the selective absorption of propene by KI−Br_2 solution [13]. This solution had several advantages over solutions of $KMnO_4$ [9] and $HgSO_4$ [14], as we showed in checks with artificial mixtures. Gaseous mixtures of ethylene and cyclopropane were analyzed with the aid of 87% sulfuric acid. In the case of mixtures of ethylene, propene, and

cyclopropane, in one portion of the gas propene and cyclopropane were absorbed with 87% H_2SO_4, and then ethylene was absorbed with bromine water; in another portion ethylene and propene were absorbed with KI-Br_2 solution, and then cyclopropane was absorbed with 87% sulfuric acid. On absorption with KI-Br_2 solution somewhat low values (by 1-2%) were obtained for cyclopropane.

TABLE 1

Serial No. of		Amt. passed (liters) of		Reaction temp. (°C)	Yield of liquid hydrocarbons		Cyclopropane that reacted (%)
Catalyst	Expt.	Ethylene	Cyclopropane		(% by wt. on original ethylene)	(% by wt. on cyclopropane that reacted)	
1-1	5	9.4	0.7	200	<1	43	14
1-2	6	7.1	1.5	250	<1	9	20
1-2	7	6.7	2.8	300	<1	21	7

TABLE 2

Serial No. of		Amt. passed (liters) of		Reaction temp. (°C)	Yield of liquid hydrocarbons		Cyclopropane that reacted (%)
Catalyst	Expt.	Propene	Cyclopropane		(% by wt. on original propene)	(% by wt. on cyclopropane that reacted)	
1-3	8	9.0	2.4	200	0.0	0.0	8.3
1-3	9	7.5	2.0	250	0.0	0.0	5.0
1-3	10	8.0	2.1	300	<0.5	26	4.8
1-4	12	0.9	5.3	200	0.0	0.0	7.5
1-4	13	0.8	4.5	250	0.0	0.0	11.1
1-4	14	0.6	4.0	300	4.5	4.5	15.0

This apparatus and experimental procedure with mixtures of olefins and cyclopropane did not differ from those described previously [15]. The reactions were carried out in a flow system at atmospheric pressure with a space velocity of the original gas mixtures of about 100 hr^{-1}. When other space velocities were used a special mention will be made.

We used the following catalysts: I, a precipitated catalyst for the hydropolymerization of olefins under the action of carbon monoxide, namely cobalt on clay, described previously [16]; we took separate portions (1-4) (volume 25 ml, length of layer 25-27 cm), which were first reduced with hydrogen at 450° for five hours. II, silica gel (KSK). III, cobalt-silica gel (KSK), prepared by the impregnation of silica gel with 3% cobalt formate solution at the boil for 30 minutes; the catalyst was first treated with a stream of nitrogen at 240°. IV, aluminum silicate. V, a precipitated cobalt-aluminum silicate catalyst which was given a preliminary reduction with hydrogen at 450° for five hours and, when cool, was treated with a stream of nitrogen to displace hydrogen. For the preparation of Catalysts IV and V we used a synthetic aluminum silicate cracking catalyst in tablet form (Houdry), whose properties have been given previously [17]. For Catalysts II-V the volume was 10-15 ml.

Experiments with a Cobalt-Clay Catalyst. At 300° and lower neither ethylene nor propene gave a liquid polymerizate over this catalyst. On addition of 7-30% of cyclopropane to ethylene a liquid polymerizate was formed under similar conditions, but in very small amount, the yield being less than 1% on the original ethylene and 9-43% on the cyclopropane that reacted; the latter isomerized only to the extent of 7-20% (Table 1). In analogous experiments with propene (Table 2), the proportion of the cyclopropane that reacted was less than in the experiments with ethylene and amounted to 5-15%. Rise in the reaction temperature did not affect the extent of the conversion of the cyclopropane, but greatly affected the yield of liquid polymerizate and cracking products. Below 300° polymerization did not occur at all, and at 300-350° it occurred to the extent of not more than 4.5% on the original propene. The yield of liquid polymerizate was 4.5-26% on the cyclopropane that reacted.

The results given in Tables 1 and 2 show that on addition of cyclopropane to ethylene and propene, which do not themselves polymerize under the given conditions, either no liquid polymerizate is formed, or a liquid polymerizate is formed in extremely small amount, which is less than the amount corresponding to the cyclopropane that reacted. It is therefore difficult to establish whether the polymerizate is formed from the olefin or the

TABLE 3

Serial No. of		Original olefin	Amt. passed (liters) of			Concentration of gas %	Obtained (liters)				Yield of liquid hydrocarbons by wt. %		Cyclopropane that reacted
Catalyst	Expt		Olefin	Hydrogen	Cyclopropane		Olefin	Hydrogen	Cyclopropane	unsaturateds			
1-2	15	Ethylene	5.5	5.2	0.0	46.7	0.3	0.8	0.0	4.6	3.7	–	—
1-2	16	Ethylene	3.3	3.6	0.7	46.3	0.6	0.5	0.3	2.6	4.1	84	57.1
1-2	17	Ethylene	2.5	4.8	2.1	31.9	0.0	2.0	1.4	3.0	0.0	–	33.3

TABLE 4

Serial No. of		Amt. passed (liters) of		Reaction temp. (°C)	Yield of liquid hydrocarbons by wt. (%)		Cyclopropane that reacted (%)
Catalyst •	Expt.	Ethylene	Cyclopropane		On original propene	On cyclopropane that reacted	
IV ••	27	6.3	0.6	150	0.0	0.0	93.3
IV	28	3.9	0.1	200	0.0	0.0	100
IV	29	6.3	0.6	300	5	35	100

• Before each experiment the catalyst was treated with a stream of air at 400° for one hour.
••In expt. 27 the space velocity was 340 hr^{-1}.

cyclopropane. Hence, the polymerizing action of the latter under the conditions used is either negligible or nonexistent. It will be seen from the results that in admixture with ethylene or propene over a cobalt-clay catalyst cyclopropane is isomerized to a small extent, namely not more than 20%.

In experiments on the hydropolymerization of ethylene in admixture with hydrogen with or without an addition of cyclopropane at 200° over a cobalt-clay catalyst the yield of liquid hydropolymerizate was very small and did not exceed 4.1% on the olefin. The addition of cyclopropane did not cause any change in the yield of hydropolymerizate (Table 3). The formation of the latter in individual experiments must be attributed to slight traces of carbon monoxide in the original ethylene, for it is known [2] that even a few hundredths of one percent of carbon monoxide in an ethylene-hydrogen mixture is sufficient to bring about hydropolymerization of the ethylene. Cyclopropane reacted to the extent of 33-57%, i.e., to a much greater extent than in absence of hydrogen, which may be explained on the view that the conversion of cyclopropane into propane occurs mainly by direct hydrogenolysis of the three-membered ring and to a less extent with intermediate formation of propene. Up to now the hydrogenation of cyclopropane has been observed over Ni [18-20], Pd [19], and Pt [19, 21] catalysts.

Experiments with Catalysts Containing Silica Gel (KSK). Propene and a 13:1 mixture of propene and cyclopropane were passed over Catalyst II at 200° with a space velocity of 250 hr^{-1}. In both cases 7 liters of original gas was taken. No liquid hydrocarbons were obtained. The cyclopropane was not isomerized and was all recovered in the outgoing gas. The same was observed over Catalyst III under analogous conditions. Neither propene nor a 5.5:1 mixture of propene and cyclopropane, treated at 200° at a space velocity of 100-200 hr^{-1}, gave a liquid polymerizate, but the cyclopropane reacted to the extent of 20%.

Experiments with Catalysts Containing Synthetic Aluminum Silicate. Synthetic aluminum silicates are active in the polymerization of propene, which is in accord with data in the literature [22]; at 200° the yield of liquid polymerizate amounted to 15% on the original propene. They were found to be very active also in the isomerization of cyclopropane. Thus, over Catalyst IV (cobalt-aluminum silicate) cyclopropane, added in an amount of 20% to propene, was isomerized to an extent of 100%; moreover, the yield of liquid polymerizate also amounted to 100% on the cyclopropane that reacted. This gives reason to supposed that the polymerizate was actually formed from propene in the moment of its formation from cyclopropane.

Ethylene, unlike propene, did not polymerize in presence of aluminum silicate at 150-300°, as has been observed previously [17]. However, under these conditions cyclopropane, added to the ethylene, was isomerized over aluminum silicate (Catalyst IV) to the extent of 93% at 150° and to the extent of 100% at 200° and higher. The formation of a liquid polymerizate from mixtures of ethylene and cyclopropane was observed only at 300°, when the yield on the original ethylene was 2-5% and did not exceed 35% on the cyclopropane that reacted, i.e. only part of the propene formed from the cyclopropane could have undergone polymerization (Table 4).

Over Catalyst V, as over aluminum silicate itself, ethylene did not polymerize at 200-300°, which is in accord with previous observations [17]. Addition of about 11% of cyclopropane to the ethylene led at 200° to an extremely small, but nevertheless appreciable, yield of liquid polymer, namely 2% on the original ethylene and 10% on the cyclopropane that reacted (62.5% of the latter entered the isomerization reaction).

SUMMARY

1. In the presence of a catalyst for the hydropolymerization of olefins under the action of carbon monoxide, i.e. cobalt on clay, which is inactive in the polymerization of the lower olefins, cyclopropane in admixture with ethylene or propene is isomerized to propene at 200-300° to the extent of 5-20%. At the same time liquid polymerizate is formed in very low yield, not exceeding 40% on the cyclopropane that reacts.

2. Under the same conditions, in admixture with the same olefins and hydrogen, cyclopropane undergoes hydrogenolysis to the extent of about 50%.

3. Under the same conditions over catalysts based on synthetic aluminum silicate, which are active for the polymerization of propene, in admixture with an olefin cyclopropane is isomerized to the extent of 65-100%.

4. On passage of a mixture of propene and cyclopropane over silica gel, neither the polymerization of propene nor the isomerization of cyclopropane occurs.

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ESTERS OF PEPTIDES CONTAINING L- PROLINE AND GLYCINE

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Peptides consisting of residues of L-proline and glycine are of great interest as models of some sections of the collagen molecule which are saturated with glycine and imino acids. It is considered [1] that it is just these sections which determine the x-ray reflections for 10 A and 2.9 A which are characteristic for collagen proteins. However, the synthesis of peptides containing L-proline and glycine in a definite sequence still presents great difficulties for investigators and often demands a special approach to each separate case.

In carrying out the syntheses of peptides with a simple alternation of glycine and proline we encountered the problem of the successive addition of dimeric glycylproline or prolylglycine residues, in the form of their esters, to a suitable dipeptide or polypeptide. The need for esters dipeptides, and also of tri and tetra-peptides consisting of glycine and L-proline residues, prompted us to improve the methods of isolating these esters described in the literature in individual cases, and in some cases to develop new methods of isolation with use of particularly mild conditions for the catalytic elimination of the benzyloxycarbonyl group, of cautious hydrolysis of the ester group, special conditions for the prevention of contact of the esters with carbon dioxide and of spontaneous transformation of dipeptide esters of a condensational character, etc. Thus it was found that the preparation of the methyl ester of L-prolylglycine of glycyl-L-proline in sufficiently pure state by the usual saturation of a suspension of the corresponding dipeptide with hydrogen chloride and subsequent treatment of the resulting hydrochloride with ammonia is not possible because of the partial breakdown of the peptide link, which occurs even when there is a deficiency of hydrogen chloride present. An attempt to prepare sufficiently pure dipeptide ester by the catalytic elimination of the benzyloxycarbonyl group from the methyl ester of the benzyloxycarbonyl dipeptide in presence of hydrogen chloride was not successful because partial hydrolysis of the peptide link occurred in this case also.

The use of catalytic elimination of the benzyloxycarbonyl group in presence of acetic acid leads to the preparation of a product of good chromatographic purity, but to obtain an analytically pure product it is necessary to apply distillation in a high vacuum, in the course of which much (70%) of the product is lost because of the cyclization of the ester into its anhydride. Hence, to prepare L-prolylglycine methyl ester in quantitative yield and in an analytically and chromatographically pure state we eliminated the benzyloxycarbonyl group over a palladium catalyst in a neutral medium. The catalyst was first activated with hydrogen chloride. If a suitable amount of catalyst is used, hydrogenation is very rapid (Fig. 1), which is very important when the strong tendency for L-prolylglycine methyl ester to undergo cyclization is considered. Thus, we found that this ester can be used as a dimer in the peptide synthesis [2]. This cannot be said of glycyl-L-proline methyl ester, which cyclizes almost instantly into the anhydride, as noted previously [3]. It is therefore obvious that to use it as a dimer in the peptide synthesis it is necessary to employ its hydrochloride. As stated above, the prolylglycine link was found to be insufficiently stable in an acid medium, but it suffered still more decomposition under conditions of alkaline hydrolysis, e. g. in the hydrolysis of the ester grouping in the benzyloxycarbonyl peptide. A remarkable feature here was the difference in the strengths of the peptide links in the methyl esters of benzyloxycarbonylglycyl-L-proline and benzyloxycarbonyl-L-prolylglycine.

Whereas in the hydrolysis of the first compound with 1 NaOH for one hour no appreciable scission of the peptide link can be observed, under these conditions the second compound undergoes considerable breakdown

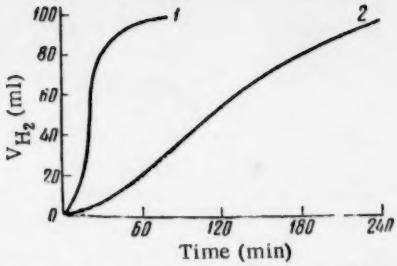

Fig. 1. Kinetics of the absorption of hydrogen in catalytic hydrogenation over a palladium catalyst: 1) absorption of H_2 in hydrogenation over a palladium catalyst activated with HCl in a neutral medium; 2) absorption of H_2 in hydrogenation over a palladium catalyst in a neural medium.

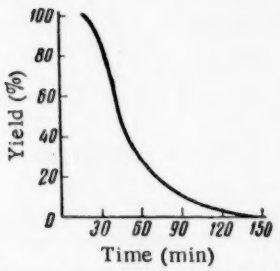

Fig. 2. Relation of yield of L--prolylglycine to time of hydrolysis of benzyloxycarbonyl--L-prolylglycine methyl ester with 1 N NaOH in dioxane (1: : 1) at 18-20°.

(up to 70%) with formation of benzyloxycarbonylproline and glycine (Fig. 2). Search for more satisfactory conditions for the hydrolysis of benzyloxycarbonyl-L-prolylglycine ester showed that the ester grouping must be removed under milder conditions than those indicated in the literature [3]; in particular, it goes well in 0.1 N NaOH (in 94% yield).

The high sensitivity of the peptide link between proline and glycine in an alkaline medium is, in our opinion, a specific character of these amino acids which begins to show itself particularly strongly in peptides consisting of simple alternations of proline and glycine. Thus in the hydrolysis of benzyloxycarbonyl-L-prolylglycyl--L-proline with 0.05 N NaOH at 20°, the appearance of benzyloxycarbonyl-L-prolylglycine and proline can be detected already after five minutes. The hydrolysis of benzyloxycarbonyl-L-prolylglycyl-L-prolylglycine methyl ester shows that it is doubtful whether it is possible to prepare the benzyloxycarbonyl tetrapeptide in a satisfactory state of purity without the use of special means of purification. The possibility of preparing benzyloxycarbonyl di- and tetrapeptide by means of alkaline hydrolysis is clearly due to the effect of the benzyloxycarbonyl group, which stabilizes a neighboring peptide linkage to some extent; in the case, however, of the hydrolysis of a benzyloxycarbonyl tetrapeptide methyl ester its effect grows appreciably weaker along the length of the peptide, which leads to a certain degree of equivalence between the peptide linkages under the conditions of alkaline hydrolysis.

It seems to us that the instability of such peptides, as compared with peptides of other amino acids, is a serious obstacle to the isolation of such sequences from collagen, even in the form of fragments of short length, when the usual methods of hydrolysis are used. The fact that in acid and alkaline hydrolysis [4,5] no peptides with such sequences are isolated may be explained either by the view that such sequences exist but are mainly broken up in the hydrolysis, or by the view that they do not in general occur, but proline, or imino acids in general occur together with glycine in another, hydrolytically more "stable", sequence.

In the course of the synthesis of the dipeptides we improved the method of preparing the acid chloride of benzyloxycarbonylglycine, which we obtained in quantitative yield. The method described in the literature [6] for the synthesis of this compound gives a low yield, and the product contains many impurities, which are troublesome in further work with the substance. An essential feature of our method is the use of mild temperature conditions at all stages of the preparation (temperature not above -10°); it is not important, however, to take the special precautions for the exclusion of moisture which are demanded by the existing method [6].

EXPERIMENTAL

For the synthesis of peptides consisting of residues of glycine and L-proline we used L-proline isolated from gelatin hydrolyzate by the known "rhodanilate" method [7] in 12% yield; $[\alpha]^{20}_D = -86.5°$ (c = 1.00 in water). The chromatographic investigation of the dipeptides and their derivatives were carried out in the system butyl alcohol–acetic acid–water (4: 5: 1). The chromatograms were developed with tolidine. "Leningrad Type B" paper was used.

Acid Chloride of Benzyloxycarbonylglycine. The synthesis of the acid chloride of benzyloxycarbonyglycine by the method given in the literature [6]gives a low yield and gives a product containing many impurities. A search for more favorable conditions in this synthesis led to the establishment of the fact that the preparation demands the observance of very mild temperature conditions. The optimum conditions for this synthesis were found to be the following. Benzyloxycarbonylglycine (18.9 g) and PCl_5 (20.4 g) were suspended in dry ether (100 ml) at 0° until a clear solution was obtained (40-60 minutes). The solution was cooled to -10° and filtered rapidly from a slight excess of PCl_5 into a receiver cooled to -10°. The filtrate was poured with stirring into 550-600 ml of petroleum ether (b.p. 30-60°) cooled previously to from -60° to -70° (acetone and solid carbon dioxide). The formation of a crystalline precipitate was observed, and this was rapidly filtered off on a funnel cooled with solid carbon dioxide and again dissolved in 100-150 ml of dry ether cooled to from -5° to -10°; the clear solution was again poured into 600 ml of petroleum ether cooled to from -60° to -70°; the precipitate crystals (leaves) were filtered off, washed with cold isopentane, and dried, first for 30 minutes in solid carbon dioxide at 1.0-0.1 mm, and then for 30 minutes at -10° at the same residual pressure; the yield of acid chloride was quantitative; m. p. 42-43°. The substance is relatively stable to moisture and may be kept in dry carbon dioxide for 12-20 hours without appreciable change.

Benzyloxycarbonylglycyl-L-proline. To a vigorously stirred solution of 8.5 g of L-proline in 45 ml of 2 N NaOH at -10° 35 ml of 2 N NaOH and 17 g of the acid chloride of benzyloxycarbonylglycine were added in portions over a period of one hour; the acid chloride was added in such a way as not to create a large excess (pH 8-9); the temperature was then raised to -5° and maintained at this level for 20-30 minutes; the solution was filtered at room temperature. The filtrate was acidified with 5 N HCl to Congo Red, and the oil that separated crystallized in needles when rubbed out and cooled; we isolated 19.2 g (85%) of benzyloxycarbonylglycyl-L-proline, m.p. 156-157° (from water).

Benxyloxycarbonylglycyl-L-proline Methyl Ester. Ethyl chloroformate (0.438 ml) was added to a solution of 0.975 g of benzyloxycarbonylglycine in 5 ml of dry chloroform containing 0.65 ml of triethylamine at the -10° to -15°; the mixture was kept for 30 minutes at this temperature and 10-15 minutes at from -3° to -5°; it was then cooled to from -10° to -15°, and a cooled solution of 0.77 g of L-proline methyl ester in 5 ml of dry chloroform containing 0.65 ml of triethylamine was added. Vigorous evolution of carbon dioxide was observed. The reaction mixtue was kept for 30 minutes at from -10° to -15°, 15 minutes at 0°, and 90 minutes at about 20°, after which it was heated rapidly to 50° (10-15 minutes). It was then extracted successively with water (one portion of 5 ml), 1 N HCl (one portion of 3 ml), 0.5 N $NaHCO_3$ (two portions of 3 ml), and water (one portion of 5 ml), it was dried with anhydrous sodium sulfate, and solvent was vacuum-distilled off. We isolated 1 g (87%) of benzyloxycarbonylglycyl-L-proline methyl ester as a yellowish noncrystallizing oil. Found: C 59.57; H 6.33; N 8.06; $-OCH_3$ 9.74%. $C_{16}H_{20}N_2O_5$. Calculated: C 60.00; H 6.25; N 8.70; $-OCH_3$ 9.7%.

Hydrolysis of Benzyloxycarbonylglycyl-L-proline Methyl Ester. To a solution of 0.4 g of benzyloxycarbonylglycyl-L-proline methyl ester in 4 ml of dioxane we added 4 ml of 1 N NaOH, and the mixture was left at about 20° for one hour; it was then filtered, acidified with 5 N HCl, and extracted with chloroform. Vacuum evaporation of the solvent left 0.36 g of oil, which crystallized when heated with water and cooled. This gave 0.34 g (97%) of benzyloxycarbonylglycyl-L-proline, m.p. 154-156°.

Glycyl-L-proline. Benzyloxycarbonylglycyl-L-proline (3.44 g) was hydrogenated as a solution in 48 ml of methanol containing 1.5 ml of water and 1.5 ml of glacial acetic acid in presence of 1 g of palladium catalyst. The carbon dioxide liberated was absorbed with sodium hydroxide. In the course of 30-40 minutes an equimolecular (to 3.44 g of benzyloxycarbonylglycyl-L-proline) amount of hydrogen was absorbed. The solution was filtered from the catalyst, and to the stirred filtrate, which was cooled to 0°, ether was added slowly until the solution just showed slight turbidity; in the course of 1-1.5 hours the precipitation of crystalline glycyl-L-proline was complete; the crystals were filtered off and dried at 56° over phosphorus pentoxide. We isolated 1.72 g (89.5%) of glycyl-L-proline, m.p. 184° (decomp.); $[\alpha]_D^{20} = -112°$ (c = 1.00 in water); Rf = 0.24.

Glycyl-L-proline Methyl Ester Hydrochloride. a) A solution of 0.5 g of glycyl-L-proline in 5 ml of absolute methanol was saturated with dry hydrogen chloride at about 20° and then for five minutes at 0°; the solution was left for 12 hours, and solvent was then vacuum-distilled off; saturation was repeated. The resulting oil was dissolved in methanol and solvent was distilled off; this was repeated twice; the residue was dried at 50-60°. We obtained 0.643 g (99.5%) of glycyl-L-proline methyl ester hydrochloride in the form of a colorless resinlike material, which was readily ground into a hygroscopic powder; Rf = 0.386. The chromatogram, which was developed

with tolidine, showed the presence of slight impurity of $R_f = 0.276$. Found: C 42.00; H 6.92%. $C_8H_{15}O_3N_2Cl$. Calculated: C 43.3; H 6.78%.

b) Benzyloxycarbonylglycyl-L-proline methyl ester (1 g) was hydrogenated as a solution in 20 ml of methanol containing 1 ml of concentrated hydrochloric acid in presence of a palladium catalyst. Catalyst was filtered off, the filtrate was vacuum-evaporated, and we obtained 0.64 g (90%) of glycyl-L-proline methyl ester hydrochloride similar in purity to the sample obtained above (a).

Glycyl-L-proline Ethyl Ester Hydrochloride. Glycyl-L-proline ethyl ester hydrochloride was prepared similarly to the methyl ester in 95% yield as a hygroscopic friable resinlike substance, $R_f = 0.335$. The chromatogram showed the presence of slight impurity of $R_f = 0.244$. Found: C 45.0; H 7.0%. $C_9H_{17}N_2O_3Cl$. Calculated: C 45.8; H 7.2%.

Glycyl-L-proline Anhydride. a) Dry chloroform (20 ml) saturated at 0° with dry ammonia together with 10 ml of ether was added to a solution of 1 g of glycyl-L-proline methyl ester hydrochloride in 15 ml of dry chloroform; the solution was filtered, and the filtrate was vacuum-evaporated at 20°. We obtained 0.61 g (90%) of gylcyl-L-proline anhydride, m.p. 203-204°, $[\alpha]^{20}_D = -217.4°$ (c = 1.0 in water). b) Glycyl-L-proline anhydride was prepared similarly from glycyl-L-proline ethyl ester hydrochloride in 85-90% yield.

Benzyloxycarbonyl-L-proline. Benzyloxycarbonyl-L-proline was prepared by a known method [8] in quantitative yield and in a pure state, this achieved by the use of pure L-proline and freshly distilled benzyl chloroformate [b.p. 35-38° (0.1 mm)]. Simultaneous addition was made over a period of 50-60 minutes of 16.3 g of benzyl-chloroformate and 22 ml of 4 N NaOH to a solution of 10 g of L-proline in 22 ml of 4 N NaOH at 0°; the reaction mixture was extracted with ether (three portions of 20 ml), filtered, and acidified to Congo Red with 5 N HCl. The aqueous layer was poured from the precipitated oil and extracted with ethyl acetate (ten portions of 40 ml); the oil and ethyl acetate extract were mixed, and the solution was dried and vacuum-evaporated at 50°. The residual oil amounted to 23 g and was dissolved with slight warming in 20 ml of carbon tetrachloride; solvent was vacuum-evaporated away. The residue was dried at 50-60° (0.1-1 mm); the oil crystallized with evolution of heat. We obtained 21.3 g (99%) of benzyloxycarbonyl-L-proline, m.p. 74-75°. The product was again dissolved in 18 ml of carbon tetrachloride, and after several hours crystallization was complete. We obtained 19.46 g (90.5%) of product, m.p. 76-77°. If the purity of the product is inadequate, it must be precipitated from its solution in petroleum ether [8].

Benzyloxycarbonyl-L-prolylglycine Methyl Ester. Ethyl chloroformate (1.4 ml) was added to a solution of 3.61 g of benzyloxycarbonyl-L-proline in 10 ml of dry chloroform containing 2.9 ml of triethylamine at from -10° to -15°; the mixture was then kept for 30 minutes at -10° and for 10-15 minutes at from -5° to -3°. The solution was then cooled from -10° to -15° and addition was made of a cooled solution of 1.8 g of glycine methyl ester hydrochloride in 10 ml of dry chloroform containing 2.9 ml of triethylamine. There was a vigorous evolution of carbon dioxide. The reaction mixture was stirred for 30 minutes at -10°, for 15 minutes at 0°, for 90 minutes at 20°, and for 10 minutes at 50°; the solution was extracted with water (one portion of 10 ml), 1 N HCl (one portion of 8 ml), 0.5 N $NaHCO_3$ (two portions of 8 ml), and water (one portion of 10 ml); it was dried with anhydrous sodium sulfate. Solvent was vacuum-distilled off and we obtained 4.3 g (96.5%) of benzyloxycarbonyl-L-prolylglycine methyl ester as a colorless oil, n_D^{20} 1.5343. Found: C 59.52; H 6.33; N 8.18%. $C_{16}H_{20}N_2O_5$. Calculated: C 60.00; H 6.25; N 8.75%.

Benzyloxycarbonyl-L-prolyglycine Ethyl Ester. Benzyloxycarbonyl-L-prolylglycine ethyl ester was prepared similarly to the methyl ester in 93% yield as a light-colored oil, n_D^{20} 1.5280. Found: C 60.5; H 6.4; $-OC_2H_5$ 12.9%. $C_{17}H_{22}O_5N_2$. Calculated: C 61.1; H 6.6; $-OC_2H_5$ 13.5%.

Benzyloxycarbonyl-L-prolylglycine. To a solution of 6.43 g of benzyloxycarbonyl-L-prolylglycine methyl ester in 25 ml of dioxane we added 20 ml of 1 N NaOH; the mixture was filtered, and 20 minutes after the addition of the sodium hydroxide it was acidified to Congo Red with 5 N HCl. The precipitated oil was extracted with ethyl acetate (200-250 ml), and the solution was dried with anhydrous sodium sulfate and vacuum-evaporated; this gave 6.1 g of oil, which was dissolved in 20 ml of chloroform and extracted with 10% aqueous potassium bicarbonate; the aqueous extract was acidified to Congo Red with 5 N HCl; the precipitated oil was extracted with ethyl acetate (200 ml); the extract was dried with anhydrous sodium sulfate and vacuum-evaporated. We isolated 5.35 g of benzyloxycarbonyl-L-prolylglycine as a friable resinlike solid, which could not be persuaded to form crystals. Found: C 58.03; H 6.05; N 9.15%. $C_{15}H_{18}O_5N_2$. Calculated: C 58.80; H 5.90; N 9.16%. In the hydro-

lysis, 0.1 N NaOH can be used equally successfully when the volume taken is increased from 20 ml to 200 ml. Hydrolysis for one hour with 1 N NaOH under the above-stated conditions leads to breakdown of the peptide linkage in both the ethyl and methyl ester of benzyloxycarbonyl-L-prolylglycine. On hydrogenation of the hydrolysis product only 30% of L-prolylglycine is isolated (Fig. 2).

L-Prolylglycine. To a solution of 3.51 g of benzyloxycarbonyl-L-prolylglycine in 60 ml of methanol addition was made of 60 ml [of water?(omitted in original—Publisher)] containing 2 ml of glacial acetic acid; the substance was hydrogenated over 1 g of palladium. After the absorption of the calculated amount of hydrogen (carbon dioxide was absorbed with sodium hydroxide), for which 20-40 minutes was required, the solution was filtered and vacuum-evaporated. We obtained 1.96 g (90.5%) of crystalline L-prolylglycine in the form of its monohydrate, m.p. 236° (decomp.). It crystallized in needles from water:methanol; $[\alpha]^{17}D = -19.8°$ (c = 4.0 in water). Found: C 43.80; H 7.32; N 14.76%. $C_7H_{12}O_3N_2 \cdot H_2O$. Calculated: C 44.21; H 7.37; N 14.74%. On the chromatogram the substance gave a blue color with isatin.

Activation of the Palladium Catalyst. Catalytic palladium (2 g), prepared by the usual method, was suspended for 10-15 minutes in 250 ml of distilled water containing 1-0.5 ml of concentrated hydrochloric acid, filtered off, washed with 25-50 ml of water, subjected to slight suction on the filter, and then immediately used for hydrogenation (Fig. 1).

L-Prolylglycine Methyl Ester Hydrochloride. a) A solution of 0.71 g of L-prolylglycine in 7 ml of methanol was saturated with dry hydrogen chloride for ten minutes at 0° and for ten minutes at 20°; it was then left for 12 hours; solvent was distilled off, and saturation with hydrogen chloride was repeated; the solution was again left for 12 hours at 20°; crystallization of glycine methyl ester hydrochloride was observed. Two spots were found on the chromatogram of the product: the main spot, which corresponded to L-prolylglycine methyl ester hydrochloride, had Rf = 0.34, and the impurity, which corresponded to glycine methyl ester hydrochloride, had Rf = 0.23. b) Benzyloxycarbonyl-L-prolylglycine (2 g) was hydrogenated over 1 g of palladium as a solution in 40 ml of methanol containing 1 ml of 34% HCl until the calculated amount of hydrogen had been absorbed; the catalyst was filtered off and solvent was distilled off at 10° under reduced pressure. We isolated 1.2 g of L-prolylglycine methyl ester hydrochloride as a light-yellow oil. It was identified chromatographically as L-prolylglycine methyl ester hydrochloride (Rf = 0.34) with a little glycine methyl ester hydrochloride (Rf = 0.22) as impurity.

L-Prolylglycine Ethyl Ester Hydrochloride. L-prolylglycine ethyl ester hydrochloride was prepared like the hydrochloride of the methyl ester both by method (a) and by method (b); the product contained glycine ethyl ester hydrochloride as impurity.

L-Prolylglycine Methyl Ester. a) Benzyloxycarbonyl-L-prolylglycine methyl ester (9.95 g) was hydrogenated as a solution in 100 ml of methanol over a palladium catalyst activated with hydrochloric acid (carbon dioxide was absorbed with sodium hydroxide). After 30-40 minutes the calculated amount of hydrogen had been absorbed; the solution was filtered, and solvent was distilled off under reduced pressure at 5° for 1-1.5 hours; the resulting oil was dried for 10-15 minutes at 20° (0.1 mm) We obtained 5.73 g of L-prolylglycine methyl ester as a colorless mobile oil, chromatographically free from impurities; b.p. 108-110° ($2.4 \cdot 10^{-5}$); $n^{17}D$ 1.4946; Rf 0.41. Found: C 50.99; H 7.56; N 15.01%. $C_8H_{14}N_2O_3$. Calculated: C 51.60; H 7.58; N 15.05%.

b) By the hydrogenation of benzyloxycarbonyl-L-prolylglycine methyl ester over the usual palladium catalyst in presence of acetic acid we again obtained a good yield of L-prolylglycine methyl ester, but in this case it was necessary to distill the product, which lowered the yield to 30% because of cyclization of the ester.

L-Prolylglycine Ethyl Ester. L-Prolylglycine ethyl ester was prepared similarly to the methyl ester in quantitative yield from benzyloxycarbonyl-L-prolylglycine ethyl ester; b.p. 126-130° (0.02 mm); $n^{21}D$ 1.4868; Rf = 0.575. Found: C 54.57; H 8.12; N 14.00%. $C_9H_{16}N_2O_3$. Calculated: C 54.3; H 8.04; N 14.05%

Hydrolysis of Benzyloxycarbonyl-L-prolylglycyl-L-proline Methyl Ester. To a solution of 0.18 g of benzyloxycarbonyl-L-proline methyl ester [2] in 2 ml of dioxane we added 4 ml of 0.1 N NaOH; the mixture was kept for five minutes at 20°, acidified to Congo Red with 0.1 N HCl, and extracted with ethyl acetate. The extract was dried with anhydrous sodium sulfate and vacuum-evaporated. We obtained 0.17 g of oil, which was dissolved in 10 ml of methanol containing ten drops of water and the same amount of glacial acetic acid. The solution was hydrogenated over 0.2 g of palladium; the catalyst was filtered off, and solvent was vacuum-evaporated away. We isolated 0.13 g of a light-yellow solid, the chromatography of which gave, in addition to the main product,

which was L-prolylglycyl-L-proline methyl ester ($R_f = 0.45$), also L-prolylglycyl-L-proline ($R_f = 0.34$) and L-prolylglycine ($R_f = 0.25$).

SUMMARY

1. The high lability of peptide linkages in peptides containing glycine residues together with some L-proline residues was demonstrated.

2. Methyl esters of dipeptides consisting of glycine and L-proline were synthesized.

3. Methods of isolating proline-containing peptide esters and of preparing benzyloxycarbonylglycine hydrochloride were perfected.

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BRIEF COMMUNICATIONS

PREPARATION OF PHENYLBORON DIBROMIDE BY DIRECT SYNTHESIS

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No methods for the preparation of organoboron compounds by the direct reaction of halogen compounds with elementary boron are described in the literature. There is only the case of the direct replacement of hydrogen in an aromatic nucleus ("boronization") and the formation of phenylboron dichloride, which was observed by Pace [1], who passed benzene vapor and boron trichloride over Pt- or Pd-asbestos at 500-600°. Phenylboron dibromide was obtained by the reaction of boron tribromide with diphenylmercury [2].

In the present communication, we describe a method of preparing phenylboron dibromide by the reaction of bromine and benzene with elementary boron according to the equation:

$$C_6H_6+B+1\frac{1}{2}\,Br_2 \xrightarrow{Ni} C_6H_5BBr_2+HBr$$

Nickel on kieselguhr was used as the catalyst. A series of side reactions occurred in addition to the given reaction.

TABLE

Substance	Chemical formula	B.p., °C (p in mm Hg)	M.p., °C	Molecular weight	
				Calculated	Found
Benzene	C_6H_6	80	—	78	77,5
Boron tribromide	BBr_3	90,6	—	250,58	253,1
Bromobenzene	C_6H_5Br	156	—	157	155,8
Phenylboron dibromide	$C_6H_5BBr_2$	89—91(14)	32—34	247	242,3
Dibromobenzene	$C_6H_4Br_2$	225	87—88	236	230,6

Substance	Yield, %	Calculated, %				Found, %			
		C	H	B	Br	C	H	B	Br
Benzene	23,4	—	—						
Boron tribromide	12,5	—	—	4	96	—	—	4,8	95,2
Bromobenzene	28,8	45,8	3,2	—	51	45,4	3,4	—	51,2
Phenylboron dibromide	21	30	1,7	4,2	63,8	29,16	2,0	4,63	64,4
Dibromobenzene	15,3	30,5	1,7	—	67,8	31,2	2,3	—	66,5

EXPERIMENTAL

The apparatus for the direct synthesis consisted of a quartz reaction tube, 600 mm long and 22 mm in diameter, a Balandin two-component burette, a receiver with a condenser, and two spiral traps cooled with dry ice.

Benzene and bromine in a molar ratio of 1:1 from the burette were passed through the reaction tube at a rate of 20 g/hr. The reactor was filled with a well-mixed powdered mass of elementary boron and nickel on kieselguhr in a ratio of 75: 25, which had first been reduced in a stream of hydrogen. The temperature in the reactor was kept at 500-525°. The reaction was carried out in a gentle stream of carefully purified nitrogen. A light brown liquid was collected in the receiver and this was then distilled. Distillation yielded fractions, some of whose physicochemical properties are given in the table.

Phenyboron dibromide is a colorless liquid with b.p. 89-91° (14 mm) and m.p. 32-34°, which has a sharp odor and fumes in air. Traces of diphenylboron bromide were detected.

SUMMARY

A method is proposed for the first time for preparation of phenylboron dibromide by direct reaction of elementary boron with bromine and benzene in a yield of more than 21%.

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DEHYDRATION OF TETRAHYDROPYRAN OVER TiO_2–Al_2O_3

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Previously [1] one of us investigated the possibility of preparing cyclopentadiene from heterocyclic compounds containing five carbon atoms in the molecule. It was found that tetrahydrosylvan and α-methyl-thiophan are converted into cyclopentadiene in a yield of ~ 20% at 600°, a pressure of 30-35 mm, and a space velocity of 1 hr^{-1} in contact with TiO_2–Al_2O_3 (5 mole %). The relation of the yield of cyclopentadiene and piperylene from tetrahydrosylvan to the space velocity at 600° on titanoalumina catayst was also investigated.

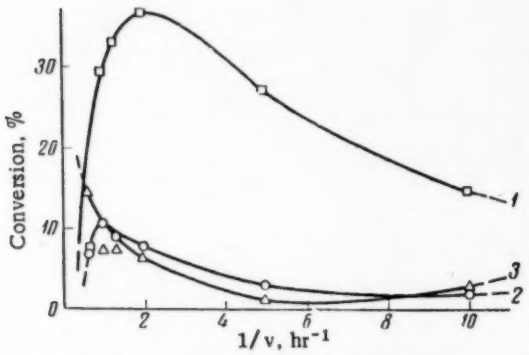


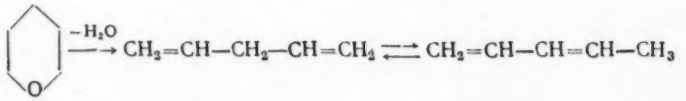
Fig. 1. Relation of piperylene (1), cyclopentadiene (2), and 1,4-pentadiene (3) yields to the reciprocal of the space velocity of tetrahydropyran at 600° on TiO_2–Al_2O_3.

The best yield of cyclopentadiene was obtained with a space velocity close to 1 hr^{-1} and of piperylene at 0.2 hr^{-1}. It was shown that the formation of cyclopentadiene and piperylene from tetrahydrosylvan proceeds both in parallel and consecutively. In contact with the same TiO_2–Al_2O_3 at 600°, piperidine gave only traces of cyclopentadiene and only traces of this hydrocarbon were found in the products from the conversion of α-methyl-pyrrolidine under the same conditions.

We investigated the dehydration of tetrahydropyran on TiO_2–Al_2O_3 (8 mole % of Al_2O_3) and the relation of the yields of cyclopentadiene and pentadienes to the space velocity and temperature (Figs. 1 and 2). The relation of the conversion of tetrahydropyran to cyclopentadiene and piperylene to the space velocity at 600° was found to be qualitatively the same as in the case of tetrahydrosylvan, but the maximum yield of cyclopentadiene and piperylene was considerably lower: the respective yields were 10.2 and 36.6% at 600° and a space velocity of 1 hr^{-1}.

It is noteworthy that on the curve of the temperature dependence of tetrahydropyran conversion (Fig. 2), the maximum cyclopentadiene yield lay at lower temperature, namely, ~400°. The piperylene yield increased with an increase in temperature and reached a practically constant value at high temperatures.

Piperylene is evidently obtained as a result of isomerization of 1,4-pentadiene, one of the products from the dehydration of tetrahydropyran:



Thermodynamic calculations on the equilibrium from the data of Kilpatrick et al. [2] show that over the temperature range studied (350-600°), 90-95% of 1, 4-pentadiene may be converted into piperylene. The low content of 1, 4-pentadiene in the catalyzate indicates that its isomerization to piperylene proceeds at a considerable rate.

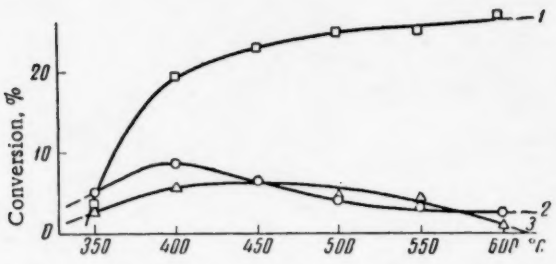
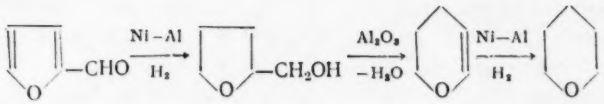


Fig. 2. Temperature dependence of the piperylene (1), cyclopentadiene (2), and 1, 4-pentadiene (3) yields in the conversions of tetrahydropyran on TiO_2–Al_2O_3 at v = 0.2 hr^{-1}.

The experimental data we obtained show that together with the isomerization of the primarily-formed 1, 4-pentadiene, there are also hydrogenation, polymerization, cracking and carbon formation. Due to this, the catalyzates contained up to 18.5% (in experiments at 600°) of 1-pentene and 2-pentene and also traces of isoprene, isoamylenes, n-pentane, and isopentane.

EXPERIMENTAL

The starting tetrahydropyran was obtained according to the following sheme:



It had the following properties: b.p. 88,5° (762.5 mm); n_D^{20} 1.4210; d_4^{20} 0.8832.

The experimental procedure and preparation of the catalyst were described in our previous article [3]. The catalyzate was analysed in the following way. The organic part of the catalyzate was separated from the aqueous part by salting out and drying over baked potassium carbonate. Its cyclopentadiene content was determined colorimetrically [4]. The fraction boiling up to 45° was then separated from it on a column with an efficiency of 20 theoretical plates. This fraction was analyzed on a gas-liquid chromatography column, 2.5 m long, packed with powdered diatomite with a grain size of 0.25-0.5 mesh, impregnated with tricresyl phosphate (30% by weight). The analysis was carried out at 20°, a hydrogen pressure of 0.25 atm and a rate of 27 ml per min.

From the head fraction boiling up to 45°, we isolated and identified as the tetrabromides 1,4-pentadiene with m.p. 86-87° and piperylene with b.p. 41.0-41.5° (740 mm); n_D^{20} 1.4310; d_4^{20} 0.6890; tetrabromide, m.p. 115-116°. From the same fraction we also isolated cyclopentadiene as the adduct with maleic anhydride which melted at 160-161°.

SUMMARY

1. We investigated the dehydration of tetrahydropyran on TiO_2-Al_2O_3 at temperatures from 350-600°, space velocities of 0.1 - 1.5 hr^{-1}, and low pressure.

2. The main products from the catalytic dehydration of tetrahydropyran under these conditions were piperylene (36.6%) and cyclopentadiene (10.2%).

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CATALYTIC SYNTHESIS OF 2,4-DI-TERT-AMYLPHENOL

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The synthesis of 2,4-di-tert-amylphenol has not been described in the literature. The patent literature [1] contains a report on its preparation by the action of a tert-amyl halide on phenol in the presence of aluminum and iron chlorides. We prepared 2,4-di-tert-amylphenol in 30% of theoretical yield by the alkylation of phenol with trimethylethylene in the presence of KU-1 cationite •. Alkylphenols, including 2,2-di-tert-amylphenol, are used as antioxidants and also as intermediates for the synthesis of insecticides and herbicides.

EXPERIMENTAL

The KU-1 cationite was first treated with 10% hydrochloric acid and washed with water until the reaction for chloride ion was negative. The alkylation was carried out in a flask fitted with a stirrer, dropping funnel, and thermometer. Into the flask were placed 47 g (0.5 mole) of phenol and 3 g of cationite (~ 6% of the weight of phenol) and the mixture heated to 60°. Trimethylethylene [b.p. 37-37.9° (742 mm); n_D^{20} 1.3878] (70 g, 1 mole) was added to the phenol dropwise. The temperature of 60° was maintained for 8 hr, and then the temperature was raised to 90°. The mixture was stirred at this temperature until trimethylethylene no longer dripped from the condenser. At the end of the reaction, the catalyst was removed by filtration and the catalyzate vacuum distilled.

In addition to a mixture of o- and p-tert-amylphenols, we obtained a 30% yield of 2,4-di-tert-amylphenol with b.p. 169-170° (22 mm); m. p. 26-27°. Found C: 81.85; 81.12; H 11.20; 11.25%. Calculated C 81.89; H 11.19%. According to the literature [1], this substance has b.p. 169-170° (22 mm) and m. p. 27°. From the 2,4-di-tert-amylphenol, we synthesized the corresponding phenoxyacetic acid: For this purpose, 1.7 g (0.03 mole) of potassium hydroxide was dissolved in 7 ml of absolute ethanol, 2.34 g (0.01 mole) of 2,4-di-tert-amylphenol added to it, and the mixture heated on a water bath. To the phenolate obtained was added 1 g (0.01 mole) of chloroacetic acid, dissolved in 5 ml of absolute ethanol. The phenoxyacetic acid formed was isolated by acidification with hydrochloric acid and then recrystallized from 20% alcohol; the yield was 30-35% of theoretical.

SUMMARY

1. 2,4-di-tert-amylphenol was obtained in a pure form by catalytic alkylation of phenol with trimethylethylene.

2. 2,4-di-tert-amylphenoxyacetic acid was synthesized.

LITERATURE CITED

1. US patent 1,972,599 (1934); Chem. Abstrs. 28, 6232 (1934).

• KU-1 cationite is a sulfonated phenol-formaldehyde resin.

ACTION OF NITRIC ACID ON THE β-GUAIACYL ETHER OF α-VERATRYL-GLYCEROL

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In a previous communication [1] we described the behavior of the lignin models, derivatives of 1-(3,4-dimethoxyphenyl)-propane and 1-(4-hydroxy-3-methoxyphenyl)-propane, under the action of nitric acid. In the present work, we continued the study of the nitration of lignin on a model, namely, a dimer. As the model we chose the β-guaiacyl ether of α-veratrylglycerol. According to the data of Adler [2], the β-guaiacyl ether of α-veratrylglycerol should be regarded as an accurate model of lignin. During ethanolysis [3], sulfite treatment [4], and oxidation with hypochlorite [5], compounds like β-aryl ethers of α-guaiacylglycerol showed properties similar to those of lignin. The coniferyl ether of 4-hydroxy-3-methoxyphenylglycerol was obtained by Freudenberg during the enzymatic synthesis of biochemical lignin from coniferyl alcohol [6].

We synthesized the β-guaiacyl ether of α-veratrylglycerol by the method of Adler, Lindgren, and Sacden [7]. The β-guaiacyl ether of α-veratrylglycerol (1 mole) was nitrated in CCl_4 with nitric acid (6 mole) at 5-6°. The reaction products were separated on silica gel. As a result we obtained a dinitro derivative of the β-guaiacyl ether of α-veratrylglycerol with the composition $C_{18}H_{20}N_2O_{10}$; molecular weight 437 (cryoscopically in benzene); m.p. 67°. Found: OH 8.00; NO_2 21.50%; $C_{18}H_{20}N_2O_{10}$. Calculation: OH 8.02; NO_2 21.7%.

Oxidation of this nitro compound with $KMnO_4$ in a weakly alkaline medium yielded 6-nitroveratric acid. Consequently, one nitro goup apparently entered each nucleus during the nitration of the β-guaiacyl ether of α-veratrylglycerol. Willstatter's nitration products of lignin, which were obtained under analogous conditions, contained ~4% of nonester nitrogen, i.e., somewhat less than one nitro group to each structural unit. The glycerol side chain of the model was unchanged during the action of nitric acid under the given conditions. During the nitration of monomers, it was observed that the alcohol group of 1-(3,4-dimethoxyphenyl)-2-propanol was more vulnerable to the oxidizing action of nitric acid than the OH groups of 1-(3,4-dimethoxyphenyl)-1- and 3-propanols. It may be assumed that etherification of the OH group in the position β to the nucleus protects it from oxidation.

Despite the presence of an alcohol group in the position α to the nucleus in the β-guaiacyl ether of α-veratrylglycerol, treatment of the dimer with nitric acid did not lead to the formation of polymers as was observed in the nitration of monomeric lignin models (guaiacyl and veratryl 1-propanols). It may be considered that during the nitration of lignin, there is no condensation due to the alcohol group in the position α to the aromatic nucleus.

EXPERIMENTAL

The β-guaiacyl ether of α-veratrylglycerol was obtained by the method of Adler, Lindgren, and Sacden according to the following scheme:

Veratrole → acetoveratrone → ω-bromo-3,4-dimethoxyacetophenone → ω-(2-methoxyphenoxy)-acetovera-

trone → α-(2-methoxyphenoxy)- β-hydroxypropio-veratrone → β-guaiacyl ether of α-veratrylglycerol.

Acetoveratrone was obtained by condensation of veratrole with acetyl chloride in the presence of $AlCl_3$ [8]; b. p. 158° (10 mm).

ω-Bromo-3,4-dimethoxyacetophenone was obtained by bromination of acetoveratrone (31 g) in chloroform at room temperature [9]. The yield was 18 g and the m. p. 81° (from chloroform + ether).

ω-(2-Methoxyphenoxy)-acetoveratrone was synthesized by condensation of ω-bromo-3,4-dimethoxyacetophenone (19 g) with guaiacol in dry acetone in the presence of K_2CO_3. The yield was 16 g and m.p. 92° (from methanol).

α-(2-Methoxyphenoxy)-β-hydroxypropioveratrone was obtained by heating ω-(2-methoxyphenoxy)-acetoveratrone (16 g) with formalin (40%) in ethanol in the presence of K_2CO_3 at 35° for 1 hr. The yield was 10.57 g and the m.p. 116° (from methanol).

The β-guaiacyl ether of α-veratrylglycerol was obtained by reduction of α-(2-methoxyphenoxy)-β-hydroxypropioveratrone (3 g) with sodium boron hydride in alcohol. The yield was 2.6 g. When dried in high vacuum, the thick, colorless sirup was converted into a glassy mass. Found: C 64.70; H 6.61; OH 9.90%. $C_{18}H_{22}O_6$. Calculated: C64.40; H 6.59; OH 10.2%.

Nitration of β-guaiacyl ether of α-veratrylglycerol. A 3-g sample of the substance was mixed with 100 ml of CCl_4. With stirring, 2.23 ml of nitric acid (sp. g. 1.52) in 50 ml of CCl_4 was added over a period of 30 min to the mixture at 6°. A resin separated on the walls of the flask and this was separated from the CCl_4 solution. The resin was dissolved in chloroform and the solution passed through a column of silica gel [10]. The CCl_4 solution of the reaction product was also passed through the same adsorbent. The adsorbents were washed with ether and then with alcohol. After evaporation under vacuum, the ether eluates gave a yellow, powdery substance in a yield of 2 g. The product was dissolved in a large amount of ether and as the latter was removed, the substance was deposited on the walls of the flask in the form of a crust. The precipitate was pressed on a Buchner funnel. This purification operation was carried out twice. The substance was dried in high vacuum. The β-nitroguaiacyl ether of α-6-nitroveratrylglycerol obtained in this way melted at 67°. Found: C 51.80; H 4.90; N 6.5 (by Dumas' method); OH 8.00; NO_2 21.5% (by reduction with subsequent diazotization). $C_{18}H_{20}N_2O_{10}$. Calculated: C 50.94; H 4.72; N 6.60; OH 8.02; NO_2 21.70%.

The hydroxyl group content was determined by Verley's method. A sample of the substance investigated was heated with a solution of acetic anhydride in pyridine for 1 hr 30 min.

SUMMARY

1. The action of nitric acid on a model of lignin, β-guaiacyl ether of α-veratrylglycerol, was studied.

2. Nitration of the β-guaiacyl ether of α-veratrylglycerol with nitric acid in CCl_4 yielded the β-nitroguaiacyl ether of α-6-nitroveratrylglycerol [1-(6-nitro-3,4-dimethoxyphenyl)-1-hydroxy-2-(nitro-2-methoxyphenoxy)-3-propanol].

3. The glycerol side chain of the dimer was unchanged during nitration under the conditions described.

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USE OF WITTIG REACTION FOR SYNTHESIZING α,β-UNSATURATED AND POLYENOIC ACIDS

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In 1955, Wittig and Haag [1] showed that boiling ethyl bromoacetate with a benzene solution of triphenylphosphine formed a phosphonium salt, which was readily converted into carbethoxymethylenetriphenylphosphorane (I) by treatment with an alcohol solution of sodium alcoholate. It was found that this phosphorane is capable of reacting analogously to the simplest methylenetriphenylphosphorane [2] and on treatment with benzaldehyde, it gives a 77% yield of ethyl cinnamate. Isler et al. [3, 4] recently perfected a method of preparing carbethoxymethylenetriphenylphosphorane and used it successfully for the synthesis of some carotinoid acids.

For synthesizing various polyenoic acids, we systematically studied the reaction of carbethoxymethylenetriphenylphosphorane (I) with different aldehydes and established that it reacts readily with saturated, unsaturated, aromatic, and heterocyclic aldehydes to give good yields of the ethyl esters of the corresponding α,β-unsaturated acids.

$$RCHO + \underset{(I)}{(C_6H_5)_3P{=}CHCOOC_2H_5} \longrightarrow RCH{=}CHCOOC_2H_5 + (C_6H_5)_3PO$$

$$CH_3(CH{=}CH)_nCHO \longrightarrow CH_3(CH{=}CH)_{n+1}COOC_2H_5 \longrightarrow CH_3(CH{=}CH)_{n+1}COOH$$

Particularly good results were obtained with polyenals for which the yields of polyenoic esters formed exceeded 80%; hydrolysis of aqueous methanol solutions of them with sodium hydroxide [5] made it possible to obtain good yields of polyenoic acids, which previously were difficultly accessible.

The table gives the yields and physical constants of the α,β-unsaturated esters we obtained and some of the corresponding acids.

In simplicity of procedure, general applicability, yields, and purity of the products formed, in most cases the Wittig reaction surpasses known methods of preparing α,β-unsaturated esters (malonic synthesis, condensation with acetoacetic ester, Reformatsky reaction, etc.) and, due to this, it is undoubtedly the most general and convenient method of synthesizing both the esters themselves and the corresponding polyene acids.

EXPERIMENTAL

Ethyl 4-phenyl-1,3-butadienecarboxylate (V). A solution of 16.06 g (0.046 mole) of carbethoxymethylenetriphenylphosphorane (I) and 2.64 g (0.02 mole) of cinnamaldehyde in 200 ml of benzene was boiled in a nitrogen atmosphere for 6 hr. The benzene was removed in vacuum, the residue treated with ligroin, the insoluble triphenylphosphine oxide removed by filtration, the solvent removed, and the residue vacuum distilled. We obtained 2.85 g of ester (V).

Esters of α,β-unsaturated acids	Yield %	Constants of esters	Notes	Lit. ref.
$C_2H_5CH=CHCOOC_2H_5$	48,5	54,5—55°(17 mm) n_D^{21} 1,4310	—	6
$C_2H_5OCH_2CH_2CH=CHCOOC_2H_5$ (III)	50	73—76°(7mm); n_D^{19} 1,4427	Found: C 62,89,62.56; H 9,09; 9,36%. $C_9H_{16}O_3$ Calculated: C 62,72; 9,36%	—
$C_6H_5CH=CHCOOC_2H_5$ (IV)	100	138—140°(10 mm) n_D^{20} 1,5591	Cinnamic acid 80%, m.p. 134—134,5°	6
$C_6H_5(CH=CH)_2COOC_2H_5$ (V)	70,5	149—151°(1 mm) n_D^{20} 1,5201	4-Phenylbutadienecarboxylic acid, 80.7%, m.p. 166-167°	6
(VI)	50,6	100°(6 mm) n_D^{17} 1,5438	Furylacrylic acid 54% m.p. 139.5-141.5°	6
$(CH_3)_2C=CH(CH_2)_2C(CH_3)=CH-CH=CHCOOC_2H_5$ (VII)	67,5	152—155°(14 mm) n_D^{20} 1,5292	—	7
$CH_2=CHCH=CHCOOC_2H_5$ (VIII)	34,1	60—61°(19 mm) n_D^{21} 1,4819	1,3-Butadienecarboxylic acid, m.p. 72°	8
$CH_3(CH=CH)_2COOC_2H_5$ (IX)	80,3	71—72°(8 mm) n_D^{21} 1,4940	Sorbic acid 81%, m.p. 131-132°, adduct with maleic anhydride, m.p. 113-115°	6
$CH_3(CH=CH)_3COOC_2H_5$ (X)	87	61—63°(0,3 mm) m.p. 39—40°	2,4,6-Octatrienecarboxylic acid 89%, m.p. 187-191°	9
$CH_3(CH=CH)_4COOC_2H_5$ (XI)	82	m.p. 93—93,5°	Found: C 74.76; 75.05; H8.06; 8.23%. $C_{10}H_{12}O_2$. Calculated: C 74.97; H 8.39%	10
$CH_3(CH=CH)_5COOC_2H_5$ (XII)	88	m.p. 135—136°	2,4,6,8-Dodecapentaenecarboxylic acid 79% m.p. 244-246°	10
$CH_3CHBrCH=CHCOOC_2H_5$	64,7	74—75°(4 mm) n_D^{20} 1,4876	Found: Br 37.82% $C_7H_{11}O_2Br$. Calculated: Br 38.64%	

By an analogous procedure, we obtained all the other esters given in the table, apart from ester (XIII). In the case of the crystalline esters (X), (XI), and (XII), it was necessary to extract them carefully with warm hexane and than recrystallize them from ethyl acetate. Ethyl β-(α'-bromoethyl)-acrylate (XIII). α-Bromopropionaldehyde (4.5 g) was added dropwise to an ice-cooled solution of 12 g of carbethoxymethylenetriphenylphosphorane in 200 ml of toluene. The mixture was kept at room temperature for 2.5 days. After removal of the solvent in vacuum, the product was treated as described above. Distillation yielded 4.3 g of ester (XIII).

2,4,6,8-Decatetraenecarboxylic acid. A mixture of 3.4 g of ethyl-2,4,6,8-dodecatetraenecarboxylate in 10 ml of methanol and a solution of 1.2 g of sodium hydroxide in 14 ml of water was boiled for 10 min and then acidified with 10% hydrochloric acid. The precipitate was collected by filtration, washed with water, and dried. We obtained 2.5 g of acid with m.p. 219-224°, which melted at 226-227° after one recrystallization from hexane [9].

The other acids listed in the table were prepared in the same way.

SUMMARY

The reaction of carbethoxymethylenetriphenylphosphorane with various aldehydes is a general method of synthesizing esters of α,β-unsaturated and polyenoic acids.

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DIENE SYNTHESIS WITH 1,4-DITHIOETHYL-1,3-BUTADIENE AND CYCLOPENTADIENE

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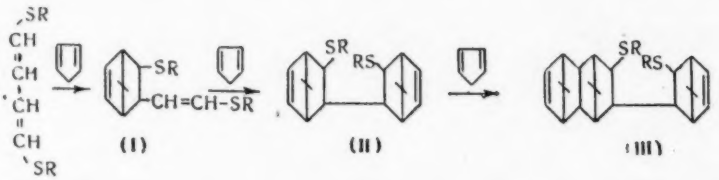
Syntheses based on diacetylene and mercaptans made it possible to prepare the following compounds, which are interesting with respect to reactivity: 1,4-dithioalkyl (aryl)-1,3-butadienes and 1-thioalkyl (aryl)-4-alkoxy-1,3-butadienes [1-5] with the general formulas RS-CH=CH-CH=CH-SR and RO-CH=CH-CH=CH-SR. Among the studied properties of the compounds synthesized, the following have been described: their capacity to change into the corresponding sulfones on oxidation [5], their decomposition by aqueous and alcohol solutions of mercuric chloride [1], their capacity to undergo diene synthesis with maleic anhydride [1, 3], and also their infrared spectra [4]. The capacity of dithioalkyl (aryl) butadienes and mixed thioethers of butadiene to undergo diene synthesis with maleic anhydride confirms that they have a diene structure.

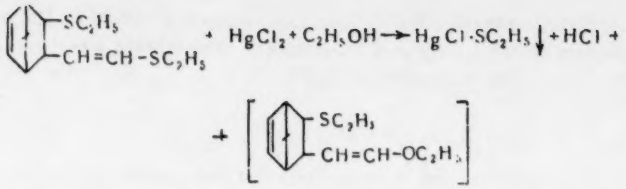
Vinyl ethers and thiovinyl ethers are known [6] to undergo diene synthesis as dienophiles. This circumstance induced us to attempt to carry out this reaction with the 1,4-substituted 1,3-butadienes we obtained as the dienophile components. For this reaction, we chose cyclopentadiene as the diene as it is most active and 1,4-dithioethyl-1,3-butadiene from among the substituted butadienes. The ratio of the starting materials and the reaction time were varied in the experiments.

The diene synthesis with 1,4-dithioethyl-1,3-butadiene and cyclopentadiene proceeded stepwise and was accompanied by the formation of adducts containing different numbers of cyclopentadiene molecules to one molecule of dithioethylbutatiene. The ratio of the adducts depended on the ratio of the starting materials and the heating time. The reaction proceeded according to the following scheme:



(I) (II) (III)

In contrast to diene synthesis with maleic anhydride, 1,4-dithioethyl-1,3-butadiene and cyclopentadiene formed adducts from which the thioethyl groups were not eliminated. Had this occurred, it would have led to aromatization of the ring [1, 3] and would have indicated that cyclopentadiene had acted as the dienophile and not our diene. We isolated three adducts from the reaction mixture. Adduct (I), which consisted of one molecule of cyclopentadiene and one molecule of the diene studied, reacted smoothly with an alcohol solution of mercuric chloride with the quantitative formation of ethylmercaptomercuric chloride and HCl, which was readily titrated with 0.1 N NaOH.



This indicated that adduct (I) contained a vinylthioethyl group and made it possible to assign to it the structure of 2-thioethyl-3-vinylthioethylbicyclo-(2,1,2)-heptene. Adduct (II) consisted of one molecule of dithioethylbutadiene and two molecules of cyclopentadiene; it did not give a characteristic reaction with an alcohol solution of mercuric chloride and therefore could be considered to be bis-[2-thioethylbicyclo-(2,1,2)-5-heptene]. Adduct (III) did not react with an alcohol solution of mercuric chloride either and corresponded in composition and constants to [1,4,5,8-diendomethylene-2-thioethyl-3-(2'-thioethyl)-bicyclo-(2', 1', 2')-5'-heptene]-2,3,4, 4a,5,8,8a-octahydronaphthalene. It should be noted that the isolation of analytically pure preparations involved great difficulties due to the formation of cyclopentadiene polymers which dissolved readily in the adducts.

EXPERIMENTAL

Reaction of 1,4-dithioethyl-1,3-butadiene with cyclopentadiene. A mixture of 15g (0.086 mole) of 1,4-dithioethyl-1,3-butadiene and 5.7 g (0.086 mole) of freshly distilled cyclopentadiene monomer was heated in a sealed ampoule on a Wood's metal bath at 170-180° for 15 hr. After removal of the cyclopentadiene polymer, the contents of the ampoule were distilled. The distillation yielded:

Fraction I with b.p. 70-77° ($2 \cdot 10^{-2}$ mm), 8.8 g; fraction II, b.p. 82-115° ($2 \cdot 10^{-2}$ mm); 2.2 g; fraction III, b.p. 20-180-190° ($2 \cdot 10^{-2}$ mm); 4.1 g; residue 0.7 g.

Fraction I consisted of the starting 1,4-dithioethyl-1,3-butadiene. After two distillations and the removal of traces of cyclopentadiene polymer, fraction II yielded adduct I (yield 25.8% of theoretical on the 1,4-dithioethyl-1,3-butadiene reacting; b.p. 149-150° (3 mm); n_D^{20} 1.5613; d_4^{20} 1.0677; Found MR 72 96; calculated $C_{13}H_{20}S_2$ 2 FMR 72.84), which was found to be 2-thioethyl-3-vinylthioethylbicyclo-(2,1,2)-5-heptene. Found: C 64.83; 64.80; H. 8.28; 8.20; S 25.90; 25.65%. Calculated: C 64.94; H 8.38; S 26.65%. Repeated fractionation of fraction III yielded adduct (II) (b.p. 127-128° ($9 \cdot 10^{-4}$ mm); n_D^{20} 1,5709; d_4^{20} 1,0774; found MR 93,45; calculated $C_{18}H_{26}S_2$ 2FMR 91,53), which was bis-[2-thioethylbicyclo-(2,1,2)-5-heptene]; the yield was 25.0% of theoretical on the 1,4-dithioethyl-1,3-butadiene reacting. Found: C 71,01; 70,93; H 8,36; 8,24%. Calculated: C 70,53; H 8,55%.

TABLE

Starting molar ratio of dithioethylbutadiene and cyclopentadiene	Heating time, hr	Yield of adducts, % of theoretical		
		I	II	III
1:1	15	25.8	25.0	28.3
1:1	10	14.5	20.0	21.8
1:2	10	19.4	31.2	13.2
2:1	18	26.1	21.5	32.3

Fraction III yielded adduct (III) with b.p. 192-193° (1.2 mm); n_D^{20} 1,5813; d_4^{20} 1,0999; found MR 112,95; calculated $C_{23}H_{32}S_3$ 2FMR 110,22. The yield was 28.3% of theoretical. Found: C 73,88; 74,12; H 8,78; 8,41%; calculated: C 74,14; H 8,65%.

From fractions II and III, we isolated an amorphous white polymer of cyclopentadiene with m.p. 179-180°. Found: C 90,22; 90,25; H 9,26; 9,24%. C_5H_6. Calculated: C 90,85; H 9,14%.

The results of experiments on the reaction of 1,4-dithioethyl-1,3-butadiene with cyclopentadiene under different conditions are given in the table. In experiments with a ratio of dithioethyl-1,3-butadiene to cyclopentadiene $\geq 1:1$, we obtained an increased amount of high-boiling residue, indicating the formation of products with an increased content of cyclopentadiene in the adduct molecule.

Titration of adduct (I) with an alcohol solution of mercuric chloride. A 0.21-g sample of adduct (I) was mixed with 0.46 g of mercuric chloride in 2.5 ml of alcohol. A white amorphous precipitate of ethylmercaptomercuric chloride formed immediately. After filtration, washing with hot alcohol, and drying, the precipitate weighed 0.25 g (96.5% of theoretical). The product did not melt at 250°. The filtrate required 8.9 ml of 0.1 N NaOH for titration in the presence of Methyl orange and this corresponds to a content of adduct (I) of 96.1%.

A 0.15-g sample of adduct (I) was mixed with 0.33 g of mercuric chloride in 1.6 ml of alcohol. We isolated 0.18 g of ethylmercaptomercuric chloride (98.0% of theoretical). The filtrate was titrated with 1.75 ml of 0.1 N NaOH, which corresponds to a content of adduct (I) of 95.4%.

SUMMARY

1. The conditions of diene synthesis with 1,4-dithioethyl-1,3-butadiene and cyclopentadiene were studied. This reaction proceeded stepwise and yielded adducts containing different numbers of cyclopentadiene molecules per molecule of dithioethylbutadiene.

2. Three adducts containing two thioethyl groups and one, two, or three endomethylenebicycloheptene rings, respectively, were isolated and characterized.

1,4-Dithioalkyl(aryl)-1,3-butadienes, which were synthesized from diacetylene and behave as typical dienes in a reaction with maleic anhydride, show dienophile properties in diene synthesis with cyclopentadiene.

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SOME α-AMINO ACIDS CONTAINING TRIFLUOROMETHYL GROUPS

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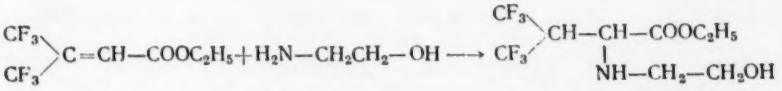
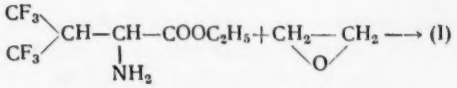
α-Amino acids containing trifluoromethyl groups have been studied very little even though the slight difference in the size of methyl and trifluoromethyl groups may not prevent fluoroamino acids from replacing normal amino acids to some extent in various processes occurring in the living organism. In addition, compounds with a trifluoromethyl group have a low toxicity in contrast to mono- and difluoromethyl derivatives. However, the only investigation of the biological activity of α-amino acids containing fluorine was described in the paper of Walborsky et al., which was published in 1955. They synthesized 5,5,5-trifluoronorvaline, 6,6,6-trifluoronorleucine, and 6,6,6-trifluoro-5-methylnorleucine and tested the action of these amino acids on the growth of some forms of bacteria [1]. We previously showed that esters of α-amino acids containing trifluoromethyl groups are obtained in good yield by the addition of ammonia and amines to β,β-ditrifluoromethylacrylic ester [2]. In the present work we studied the addition of ethanolamine and diethanolamine to this ester.

Under mild conditions, ethanolamine adds to ethyl β, β-ditrifluoromethylacrylate to form the ethyl ester of N-(β-hydroxyethyl)-hexafluorovaline (I).



(I)

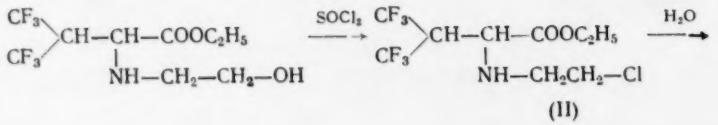
Ethanolamine reacts only through the amino and not through the hydroxyl group even though alcohols add readily to fluoroolefins, especially in an alkaline medium. The structure of the addition product was demonstrated by its synthesis from hexafluorovaline and ethylene oxide.



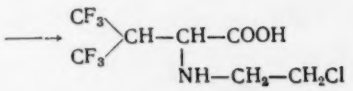
The reaction proceeded readily at room temperature in 50% acetic acid. When the ester of N-(β-hydroxyethyl)-hexafluorovaline obtained was treated with thionyl chloride, it was converted smoothly into the ester of N-(β-chloroethyl)-hexafluorovaline (II), which was hydrolyzed by hydrochloric acid to give water-soluble N-(β-chloroethyl)-hexafluorovaline (III).

These reactions could not be carried out with diethanolamine. While ethanolamine reacts with the unsaturated ester at -70°, diethanolamine does not react with it even when heated to 150° in a sealed ampoule. On the other hand, in the hydroxyethylation of hexafluorovaline, only one molecule of ethylene oxide reacted.

Neither heating not changing the solvent made it possible to introduce a second hydroxyethyl group. N-(β-Hydroxyethyl)-hexafluorovaline did not react with ethylene oxide at all. The most probable reason for the impossibility of adding diethanolamine to β,β-ditrifluoromethylacrylic ester is apparently the steric hindrance of the carbalkoxyl group to the introduction of the di-(β-hydroxyethyl)-amino group in the α position.



(II)



(III)

At the present time we are testing the biological activity of hexafluorovaline itself and its hydroxy- and chloroethyl derivatives.

EXPERIMENTAL

1. Ethyl ester of N-(β-hydroxyethyl)-hexafluorovaline (I). A mixture of 26.2 g (0.103 mole) of ethyl ester of hexafluorovaline, 100 ml of 60% acetic, and 9.5 g (0.216 mole) of ethylene oxide was kept at room temperature for 48 hr. The solution was then neutralized with dry sodium carbonate, the oily layer separated, and the aqueous layer extracted with ether. After the extract had been dried and the solvent distilled, the residue was vacuum distilled. We obtained 6 g of the original ester [b.p. 79-82° (21 mm), melting point of hydrochloride and mixed melting point 184°] and 19.0 g (81% calculated on the amino ester reacting) of (I) with b.p. 91-91.5° (1 mm); n^{20} 1,3874; d_4^{20} 1.3805; found MR 50.73; calculated MR 50.66 with AR_F 1.12. The hydrochloride had m.p. 148.5-149° (from ethyl acetate). Found: C 32.22; H 4.17; F 34.21; N 4.20%. $C_9F_6H_{14}O_3NCl$. Calculated: C 32.40; H 4.20; F 34.21; N 4.20%.

Ethanolamine (2.6 g, 0.0425 mole) was added dropwise to 10.2 g (0.05 mole) of the ethyl ester of β,β-ditrifluoromethylacrylic acid, cooled to -60°. The mixed was stirred and left for 1 hr while it heated up to room temperature. Subsequent vacuum distillation gave 11.9 g (93% of theoretical) of (I) with b.p. 89-95° (1 mm) and n_D^{20} 1.3879. The melting point of the hydrochloride and a mixed melting point were 145-146.5°.

Ethyl ester of N-(β-chloroethyl)-hexafluorovaline (II). A mixture of 14.1 g (0.047 mole) of (I), 9.0 g (0.075 mole) of thionyl chloride, and 50 ml of absolute benzene was boiled for 8 hr. The benzene was then removed by distillation, the residue treated with water, and the oil formed extracted with ether and dried. Vacuum distillation after removal of the solvent gave 11.5 g (77% of theoretical) of (II) with b.p. 82-82.5°(5 mm); n_D^{20} 1.3910; d_4^{20} 1.3820; found MR 54.24; calculated MR 54.00. The hydrochloride had m.p. 129-130° (from a mixture of ethyl acetate and carbon tetrachloride). Found: C 30.64; H 3.74; F 32.81; N 4.18%. $C_9F_6H_{13}O_2Cl_2$. Calculated: C 30.68; H 3.69; F 32.89; N 3.98%.

N-(β-Chloroethyl)-hexafluorovaline (III). A mixture of 1.6 g of (II) and 5 ml of concentrated hydrochloric acid was heated in a sealed ampoule at 100° until the amino ester hydrochloride, which was insoluble in cold water, dissolved completely. The solution was then evaporated to dryness and the residue recrystallized three times from n-octane. We obtained 1.1 g (84% of theoretical) of (III) with m.p. 145-146.5°. Found: C 29.25; H 2.70; F 39.73%. $C_7F_6H_8O_2NCl$. Calculated: C 29.17; H 2.78; F 39.60%.

SUMMARY

Ethanolamine was added to β,β-ditrifluoromethylacrylic ester and hexafluorovaline ester was hydroxyethylated. Both reactions yielded the ester of N-(β-hydroxyethyl)-hexafluorovaline, which could be used as the starting material for the synthesis of physiologically active substances.

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ORDER OF ADDITION OF DIISOBUTYLALUMINUM HYDRIDE TO DIMETHYLFULVENE

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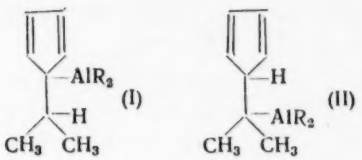
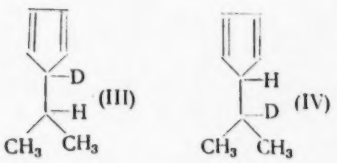
Ziegler, Fuson, Taber, and others [1-4] have shown that alkyllithiums and alkylmagnesium halides are capable of adding to the semicyclic double bond of fulvenes. In this case, the metal or residue containing the metal adds to the ring. We carried out the reaction between dimethylfulvene and diisobutylaluminum hydride. $HAlR_2$ added to the fulvene. Hydrolysis of the organoaluminum compound formed yielded isopropylcyclopentadiene, isobutane, and aluminum hydroxide. It was impossible to judge how the addition of $HAlR_2$ proceeded from the reaction product formed. This addition could proceed in two directions: 1) AlR_2 could add to the cyclopentadiene ring to form product (I) • and 2) AlR_2 could add to the isopropyl group to form product (II).



where R = i-C_4H_9.

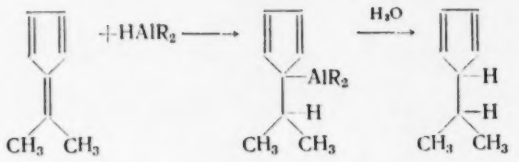
In order to determine the order of addition of $HAlR_2$ to fulvene, we used a tracer method. It was previously shown that cyclopentadiene is capable of exchanging all the hydrogen atoms for deuterium of heavy water (or deuteroalcohol) in the presence of base under very mild conditions. Hydrogens that are not bound to carbon atoms of the cyclopentadiene ring do not undergo hydrogen exchange under these conditions [5].

To solve this problem, we hydrolyzed the organoaluminum compound (I or II) with deuterium oxide. This yielded deuteroisopropylcyclopentadiene, whose structure should correspond to (III) or (IV).



• We are not considering the position of AlR_2 in the ring here. There are three theoretically possible cases where AlR_2 is in position 1, 2, or 3.

This hydrocarbon was subjected to hydrogen exchange with C_2H_5OH in the presence of C_2H_5ONa under conditions under which there is hydrogen exchange between isopropylcyclopentadiene and C_2H_5OD. In this case, there should be no hydrogen exchange with the hydrocarbon of structure (IV). With a deuteroisopropylcyclopentadiene of structure (III), isotopic equilibrium should established between the hydrogen of the alcohol and the five hydrogens of the cyclopentadiene. Experiments showed that hydrogen exchange occurred, i.e., the hydrocarbon had structure (III) and consequently the diisobutylaluminum hydride added to the semicyclic double bond in such a way that the AlR_2 added to the cyclopentadiene ring and the hydrogen added to the isopropyl group according to the following scheme:



where R = i-C_4H_9

EXPERIMENTAL

Addition of diisobutylaluminum hydride to dimethylfulvene. In a nitrogen atmosphere, 24 g of $HAl(i\text{-}C_4H_9)_2$ was placed in a four-necked flask with a stirrer, reflux condenser, thermometer, and dropping funnel and 16.5 g of dimethylfulvene was added over a period of 1 hr at 65-75°. The addition product was decomposed at 20° by the gradual addition of its ether solution to water (or D_2O). The hydroxide formed was removed by filtration and the ether solution washed and dried. Removal of the ether yielded 11.5 g (68% yield) of isopropylcyclopentadiene with b.p. 28-33° (30 mm); 38° (38 mm); n_D^{20} 1.4563; d_4^{20} 0.8165; found MR 36.06; calculated MR 36.01. Found: C 89.00; H 11.37%. $C_{18}H_{12}$. Calculated: C 88.81; H 11.18%. According to literature data [6]: b.p. 28-30° (18 mm); n_D^{20} 1.4639.

Hydrogenation of isopropylcyclopentadiene over $Pd/BaSO_4$. A 0.999-g sample of C_8H_{12} was used for hydrogenation. The amount of hydrogen absorbed was 418.5 ml (reduced to normal conditions). The amount calculated for two double bonds was 414.4 ml H_2.

Reaction of isopropylcyclopentadiene with maleic anhydride. A 1.2-g sample of isopropylcyclopentadiene was added to 1.08 g of maleic anhydride in 3 ml of benzene; the mixture was heated for an hour at 50-60° and left overnight. After removal of the benzene, 1.7 g of adduct was distilled at 143-145° (3 mm) and this had n_D^{20} 1.4980; d_4^{20} 1.1557; found MR 52.30; calculated MR 52.21. Found: C 69.93; 69.96; H 6,77; 7.75%. $C_{12}H_{14}O_3$. Calculated: C 69.88; H 6.84%.

TABLE 1*

Expt. No.	Hydrocarbon	Amount: Alcohol, ml	Amount: Na, g	Amount: Hydrocarbon g	Time, hr	Exchange, γ/ml: Calculated	Exchange, γ/ml: Experimental	% of calc.
1	Isopropylcyclopentadiene	18	0,15	1,60	17	1625	1200	74
2	The same	18	0,15	1,65	17	2375	1765	74
3	» »	18	0,15	1,43	29	2450	1680	70
4	» »	18	0,05	1,60	3	2400	1740	75
5	» »	18	0,03	1,59	2	2400	1500	62
6	Cyclopentadiene	45	0,06	4,00	2	4850	3540	73
7	»	45	0,06	4,00	4	4850	3470	72

Hydrogen exchange of isopropylcyclopentadiene. A sample of the hydrocarbon was dissolved in a solution of sodium alcoholate in C_2H_5OD. At the end of the experiment, the solution was poured into an acidified solution

* The deuterium content was determined by measuring the density of the water formed by combustion of the substance by the drop method.

of $CaCl_2$. The hydrocarbon layer was washed several times with $CaCl_2$ solution, dried, and distilled under reduced pressure. Special experiments showed that there was no isotopic exchange of hydrogen under the conditions for processing the reaction mixture. Preliminary experiments, whose results are given in Table 1, were carried out to find the conditions for hydrogen exchange.

Table 1 shows that the conditions of experiment 4 were optimal.

TABLE 2

Initial excess weight, γ/ml	Excess weight after experiment γ/ml		Difference γ/ml
	Calculated	Found	
5150	730	830	100
	125	375	150
	40	120	90
4150	600	685	85
	100	210	115
	20	95	75

It is interesting to note that in all experiments the hydrogen exchange of isopropylcyclopentadiene was not more than 75% of the calculated value, assuming that the distribution coefficient $\alpha = 1$. Hydrogen exchange of cyclopentadiene and cyclopentadieneimides with deuteroethanol reached the same value [7]. In experiments on the exchange of deuteroisopropylcyclopentadiene with alcohol, we considered the equilibrium value equal to 75% of the calculated value.

The experiment on the exchange of D-isopropylcyclopentadiene with C_2H_5OH was carried out for 3 hr. We used 18 ml of alcohol and 0.05 g of Na with 1.6 g of hydrocarbon. The hydrocarbon isolated after the exchange was again subjected to hydrogen exchange. The experimental results (Table 2) show that at least 98% of the deuterium was in the ring.

SUMMARY

The addition of $HAl(i\text{-}C_4H_9)_2$ to dimethylfulvene proceeds in such a way that the hydrogen adds to the isopropyl group and the AlR_2 to the carbon ring.

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DETERMINATION OF ELEMENTS IN TUNGSTEN SULFIDE CATALYSTS

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
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Original article submitted January 27, 1960

The ratio of S and W in tungsten catalysts (WS_2), which are widely used for destructive hydrogenation of high-boiling organic compounds under pressure [1], does not correspond to the stoichiometric value [2]. Therefore, the analysis of these catalysts is of considerable interest. At the same time, no rapid and convenient method for the determination of tungsten and sulfur and no method at all has been proposed for the determination of carbon and hydrogen in spent catalysts covered with a tarry deposit. For the determination of C and H it is not possible to use one of the dry combustion methods which are normally used in organic elementary analysis as tungstem oxides are volatile at comparatively low temperatures (500° and above). The method we propose makes it possible to determine carbon, hydrogen, sulfur, and tungsten simultaneously on one sample in 45-60 min. The method may be used for both micro and semimicro determinations. The method essentially consists of dry combustion of a thin layer of catalyst in a stream of hydrogen at 450-500°. The combustion products are trapped separately and determined gravimetrically.

EXPERIMENTAL

Determination procedure. We used an apparatus for determining carbon and hydrogen by a rapid method [3]. A sample weighing 4-25 mg was spread in a thin layer on the bottom of a quartz or platinum boat, 80 mm long, 4 mm high, and 5 mm wide. The boat was placed in a qaurtz bottle with a ground stopper (Fig. 1a), 90 mm long with an internal diameter of 6 mm. The sulfur oxides were trapped at 600° with electrolytically deposited silver in a boat [4] (Fig. 1b) the same as for the sample or somewhat wider (with the same length, a height of 5 mm, and

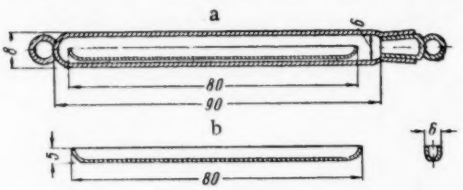

Fig. 1.

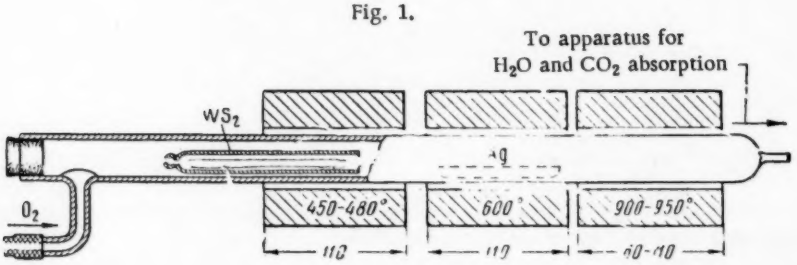

Fig. 2.

a width of 6 mm). The boat with the silver and the bottle with the sample were placed in the combustion tube as shown in Fig. 2 and the combustion carried out with the furnace gradually moved from the open end of the bottle to the closed end, i.e., against the oxygen current. The oxygen flow rate during the analysis was 15-20 ml per minute. The water and carbon dioxide were trapped in absorber apparatuses with anhydrone and ascarite in the usual way. The sulfur oxides were trapped with the silver and the tungsten oxide remained in the bottle as an ash. At the end of the combustion, which lasted for 15-20 min, the furnaces heating the bottle with the sample and the boat with the silver were removed and oxygen passed for a further 10 min. Then the absorber apparatuses for water and carbon dioxide were disconnected, the bottle and the boat with silver withdrawn from the combustion tube, and then after 15 min, the apparatus with the ascarite (CO_2), then that with the anhydrone (H_2O), next the boat with the silver (SO_4), and finally the bottle with the boat and ash (WO_3) weighed.

The C and H contents were calculated as percentages in the usual way.

$$\% S = \frac{0{,}3338 \cdot a \cdot 100}{N}, \quad \% W = \frac{0{,}7930 \cdot b \cdot 100}{N},$$

where a is the increase in weight of the boat with the silver, b is the weight of ash, and N the weight of the sample of material.

SUMMARY

A simple and rapid method is proposed for determining C, H, S, and W in tungsten sulfide catalysts. The accuracy of the determination is ± 0.3%.

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LETTERS TO THE EDITOR

N → O BENZOYL MIGRATION OF DIASTEREOISOMERIC 1,2-DIPHENYL-1-BENZOYLAMINO-3-PROPANOLS

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 8, p. 1522, August, 1960

By the reduction of α, β-diphenyl-β-aminopropionic acid [1] with $LiAlH_4$, we obtained the corresponding γ-aminopropanol, which was diastereoisomeric with that described previously [2]. Benzoylation of the new aminopropanol gave 1,2-diphenyl-1-benzoylamino-3-propanol (I) with m.p. 187-189°, while under the same conditions, its known diastereoisomer gave a benzoyl derivative (II) with m.p. 225-227°. When (I) was heated for 10 hr at 40° with 5.16 N solution of hydrogen chloride in ethanol, it rearranged into the corresponding O-benzoyl derivative; (II) rearranged under analogous conditions only when heated to 100°.

We therefore ascribed a threo configuration to (I) and an erythro configuration to (II). The high rate of the N → O benzoyl migration in (I) we explain by the trans position of the two neighbouring phenyl groups in the intermediate methoxazine, which is energetically more favorable [3], on the one hand, and by the higher content of the reactive conformation in the equilibrium mixture of conformational isomers of (I), i.e., the high value of the N_a factor in the Winstein–Holness equation $k = N_a \cdot K_a$ [4], on the other.

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CATALYTIC HYDROGENATION OF WOOD AND OTHER VEGETABLE MATERIALS

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Original article submitted May 4, 1960

The great plant wealth of the USSR needs efficient chemical utilization. We found a method of preparing from wood and other plant materials polyhydric alcohols and phenols, which are required for the production of high polymers, deemulsifiers and other surface-active substances, plasticizers, moisture stabilizers, lacquers, etc. The process consists of two successive stages: hydrolytic hydrogenation of polysaccharides [1] in an acid medium and hydrogenation of lignin [2] in an alkaline medium. The same Ru catalyst is used in the two stages [1, 2].

Example. A 5-g sample of acetone-treated pine sawdust (containing 50% of difficultly and 17% of readily hydrolyzable polysaccharides) was placed in an autoclave with 50 ml of 0.7% aqueous solution of H_3PO_4 and 0.025 g of Ru (on charcoal) [1] and heated for 45-60 min at 160-170° and 30-50 atm (initial) of H_2. The colorless catalyzate was filtered free from catalyst and lignin, passed through a column with anionite to remove H_3PO_4, and evaporated in vacuum. The concentrated mass crystallized. The crystals, which consisted of hexitols and pentitols, were obtained in 95% yield on the wood polysaccharides.

The precipitate was removed from the filter, placed in the same autoclave, and heated for 2-2.5 hr with 30 ml of 1.5% aqueous NaOH at 50-70 atm of H_2 and 280-320°. The filtered catalyzate was colorless, but became brown in air and had a strong odor of phenol. No lignin was precipitated when the catalyzate was acidified. There was no hydrocarbon layer. By paper chromatography of the azo dyes obtained by coupling with freshly diazotized sulfanilic acid solution, it was shown that the catalyzate contained m-cresol and pyrocatechol. The phenol yield was ~35% of the lignin.

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STRUCTURE OF DOUBLE DIAZONIUM SALTS

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Original article submitted May 12, 1960

Up to now it has been generally accepted that double diazonium salts of metal halides have an ionic structure $Ar-\overset{+}{N}\equiv N[MeX_{n+1}]^-$ and the metal atom is not bound chemically to the trivalent nitrogen atom.

The results of our spectroscopic study of double diazonium salts of cobalt and copper chlorides (obtained for the first time) give grounds for considering that there is actually a chemical bond between the metal atom and the terminal nitrogen of the aryl diazo group.

We studied the double salts $(ArN_2Cl)_2MeCl_2$, where Me is Co or Cu and Ar is $p\text{-}CH_3C_6H_4$, $p\text{-}ClC_6H_4$, $p\text{-}O_2NC_6H_4$, or $p\text{-}C_2H_5OOCC_6H_4$ and $ArN_2Cl \cdot MeCl_2$, where Me is Co or Cu and Ar is $p\text{-}BrC_6H_4$. The $CoCl_2$ salts were greenish blue and the $CuCl_2$ salts yellow. The ultraviolet and infrared spectra of the double diazonium salts of copper and cobalt chlorides were plotted. In the region of the triple bond, the infrared spectra showed absorption in the form of an asymmetric or split band, whose position was considerably lower than in the original aryl diazonium chloride in the same way as has already been observed with other double diazonium salts [1]. The ultraviolet spectra of methanol solution of double diazonium salts of copper and cobalt chlorides showed absorption (in the region of 27,000-28,000 cm^{-1} for cobalt salts and 18,500-20,500 cm^{-1} for copper salts), which corresponds to the band shown by copper and cobalt complexes with a nitrogen atom in the complex unit [2].

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METHOD OF SYNTHESIZING MERCAPTALS AND DIMERCAPTALS OF VARIOUS ALDEHYDES FROM THE CORRESPONDING ACETALS

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Original article submitted May 23, 1960

We studied the reaction of mercaptans with various acetals and found that it has a general character and may serve as a convenient method of synthesizing various mercaptals and dimercaptals of saturated and unsaturated aldehydes from the corresponding acetals, ether acetals, and thioether acetals. It is known [1-3] that the alkoxyl groups in acetals are labile, but there is no information in the literature on their capacity to exchange with thioalkyl radicals and this induced us to make a detailed study of the reaction described, which proceeds according to the schemes:

$$R{-}CH(OR')_2 + 2R''SH \longrightarrow RCH(SR'')_2 + 2R'OH;$$

$R' = C_2H_5$; C_4H_9; when $R = CH_3$ $R'' = C_2H_5$

$R = CH_3$; $CH_3{-}C{\equiv}C{-}$; $CH_3{-}CH(OC_4H_9){-}CH_2$ when $R' = C_2H_5$ $C_6H_5CH_2$.

$$RX{-}CH{=}CH{-}C{\equiv}C{-}CH(OR')_2 + R'SH \longrightarrow (R'S)_2CH{-}CH_2{-}C{\equiv}C{-}CH(SR')_2 \quad (I)$$

$RX = C_2H_5S$; C_4H_9O when $R' = C_2H_5$.

Thus, with heating in an ampoule at 100°, the dibutyl acetal of acetaldehyde gave an 84.2% yield of the dithioethyl mercaptal with b.p. 78.5° (16 mm); n_D^{20} 1.5022; titration with mercuric chloride showed that the sample contained 99.09% of the mercaptal. The diethyl acetal of 4-thioethylpentenynal yielded the diethyl dimercaptal of pentynal (I) with b.p. 122° (0.01 mm); n_D^{20} 1.6058. Found: C 50.93; 50.49; H 7.77, 7.80. Calculated: C 50.61; H 7.83. Titration with mercuric chloride showed that the titration sample contained 79.73% of this compound. The reaction studied makes it possible to synthesize mercaptals of various structures, whose synthesis is difficult by methods known up to now.

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

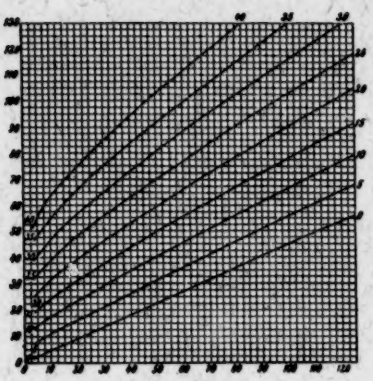
Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) } Dokl(ady) AN SSSR }	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
		Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
		Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
Life Sciences		Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
		Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
Chemical Sciences		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
		Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
Earth Sciences		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1-6	1957-1958
		Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1-6	1957-1958
Mathematics		Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
		Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
Physics		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)					
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations		1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union		1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute		1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1	1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3	1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1	1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1	1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1	1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1	1958
	Metallurg	Metallurgist	Acta Metallurgica		1	1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1	1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1	1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6	1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1	1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1	1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1	1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1	1958
PTÉ	(see Pribory i tekhn. éks.)					
	Problemy Severa	Problems of the North	National Research Council of Canada			
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1	1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1	1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1	1959
	Stal'	Stal (In English)	Iron and Steel Institute		1	1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1	1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4	1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1	1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1	1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1	1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1	1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1	1960
Usp. fiz. nauk	(see UFN)					
Usp. khim(ii)	(see UKh)					
Usp. matem. nauk	(see UMN)					
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd		48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.		4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*		1	1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*		1	1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*		1	1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1	1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1	1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i theoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1	1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7	1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1	1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1	1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1	1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1	1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1	1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1	1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1	1958

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.



TABLES AND NOMOGRAMS OF HYDROCHEMICAL ANALYSIS

by I. Yu. Sokolov

Translated from Russian

Upon completion of analytical experiments, every research chemist, whether he uses a "test tube" or a "пробирка," must calculate his findings in the international language of figures in two forms (weights and equivalents), and often three (weights, equivalents and percent-equivalents), and then compare experimental data with theoretical values.

Technicians and statisticians working with the results of hydrochemical analyses performed at different times by different laboratories inevitably face the problem of converting their figures to one system.

All such calculations are considerably simplified by the use of the tables and nomograms in this book, originally published by the State Scientific and Technical Press for Literature on Geology and the Conservation of Mineral Resources, Moscow.

All the tables and nomograms are based on analytical results expressed in the form widely used in hydrogeological practice—milligrams per liter (weight form) and milligram-equivalents per liter (equivalent form). For calculation of percent-equivalents, the sum of cation equivalents and the sum of anion equivalents are taken as 100% each. Several new tables are presented for the first time, and the many tables for converting water-analysis results from one form to another make it possible to find the milligram-equivalents for any practically possible content of a component in water, accurate to the second decimal place, and the weight content of substances to tenths of a milligram.

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II. Table for converting milligram-equivalents of Ca^{2+}, Mg^{2+} and HCO_3^- into German degrees of hardness

III. Tables for converting milligrams into milligram-equivalents

IV. Tables for converting milligram-equivalents into milligrams

V. Tables for converting oxides to ions

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VII. Table for converting milligrams of NH_3 into milligrams of NH_4^+

VIII. Table for converting oxidizability with milligrams of $KMnO_4$ into milligrams of O

Factors for converting the results of water analysis from one form into another

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Nomogram for calculating percent-equivalents

Nomogram for calculating pH from given values of free CO_2 and HCO_3^-

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